# Research Accomplishments

FOR THE

# Environmental Management Science Program

**FY2001 Mid-Year Summary**
**Volume 1: Project Accomplishments**

*Published April 2001*

***U.S. Department of Energy***
***Office of Environmental Management***
***Office of Science***

**COVER GRAPHIC:** Colloids, micron sized particles that behave as fluids and play a role in contaminant transport, formed during reaction of Hanford Sediments with simulated tank solutions [see Project #70135].

# *EXECUTIVE SUMMARY*

The Environmental Management Science Program (EMSP) was established by Congress in 1996 under the Department of Energy (DOE) Environmental Management (EM) Office of Science and Technology to "develop and fund a targeted long-term basic research program that will result in transformational or breakthrough approaches for solving the Department's environmental problems." The EMSP is a partnership between the Department of Energy (DOE) Office of Basic and Applied Research and the Office of Science, and funds competitively awarded research that seeks scientific understanding leading to reduced remediation risks, costs, or schedules, and helping to solve currently intractable problems. As such, EMSP supports research that leads directly to the fulfillment of the following EMSP research objectives:

- Provide scientific knowledge that will revolutionize technologies and clean-up approaches to significantly reduce future costs, schedules, and risks

- "Bridge the gap" between broad fundamental research that has wide-ranging applicability such as that performed in DOE's Office of Science and needs-driven applied technology development that is conducted in EM's Office of Science and Technology

- Focus the nation's science infrastructure on critical DOE environmental management problems.

The intent of this *EMSP Research Accomplishments Summary* is to provide information concerning varied research transition activities. Research transitions are measures of how successfully the program has transitioned knowledge gained from research projects to other areas. These measures may be in the form of actual transfers of new knowledge or data gained through research products or processes to other areas within EM, such as Focus Areas and Crosscutting Programs, or may be more general knowledge transfer measures found in similar research programs, such as collaborations, numbers of student researchers, peer reviewed papers and presentations (communication products), or consultations.

Since 1996, the EMSP has funded over 300 basic research projects at 90 universities, 13 national laboratories, and 22 other governmental and private laboratories in 39 states and 7 countries. Many of these projects have generated sufficient technical data and identified specific, potential field applications to warrant movement into the applied R&D arena. Research accomplishments from EMSP-funded projects, with total quantities in each category as follows:

- *Collaborations* — *Total*

| | |
|---|---|
| Consulting - provide advice or technical expertise | 42 |
| Joint interaction - researcher/end-user in joint interaction | 46 |
| Mission directed - project direction provided by end-user | 18 |
| Program interaction - researcher to researcher interaction | 53 |

| • *Student Researchers* | *Total* |
|---|---|
| Undergraduate Researchers | 73 |
| Master Researchers | 248 |
| Ph.D. Researchers | 48 |
| Post Doctoral Researchers | 156 |

| • *Research Transfers* | *Total* |
|---|---|
| Commercializations | 12 |
| Deployments | 2 |
| Field Tests | 12 |
| Focus Areas & Crosscutting Programs | 3 |
| Processes | 2 |

The information presented in this volume is an attempt to capture research transition activities as of March 30, 2001, and therefore should not be considered to be a complete or accurate listing. Research publications and other communications products for EMSP-funded projects are documented in Volume 2.

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## *Introduction*

# RESEARCH ACCOMPLISHMENTS FOR THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

## INTRODUCTION

The Environmental Management Science Program (EMSP) is a partnership between the Department of Energy (DOE) Office of Basic and Applied Research and the Office of Science. The mission of the EMSP is to develop and fund a targeted long-term basic research program that will result in transformational or breakthrough approaches for solving the Department's environmental problems. The EMSP funds competitively awarded research that seeks scientific understanding leading to reduced remediation risks, costs, or schedules, and helping to solve currently intractable problems. The sites will use the understanding gained through EMSP-supported research to improve their cleanup efforts. Implementing these approaches will lead to reductions in cleanup costs, as well as reductions in risks to workers and the public. The Environmental Management Science Program (EMSP) has funded over 300 basic research projects at 90 universities, 13 national laboratories, and 22 other governmental and private laboratories in 39 states and 7 countries. Many of these projects have generated sufficient technical data and identified specific, potential field applications to warrant movement into the applied R&D arena.

The information contained in this document has been gathered from various sources, such as interactions with EMSP staff, proceedings from EMSP workshops and technical conferences, principal investigators, the Project Tracking System, EMSP Project Annual Reports, and literature searches. The information presented is an attempt to capture research transition activities and therefore should not be considered to be a complete or accurate listing. This document contains the best available data as of March 30, 2001.

### Problem Areas Addressed by EMSP Research

The EMSP focuses on the key EM problem areas defined in the *EM Research and Development Program Plan*. These problem areas are grouped by waste area, representing the scope of cleanup facing EM. These areas are the basis for developing science and technology investments. The focus areas link both research and technology development to these eight problem areas:

- *Deactivation and Decommissioning* research advances science to solve environmental problems associated with placing equipment and structures in a desired end state. Desired end states include complete removal and remediation of the facility, release of the facility for unrestricted use, or release of the facility for restricted use.

- *High-Level Waste* research advances science to solve environmental problems associated with storage tanks containing highly radioactive wastes, which include organic and inorganic chemical compounds in solid, colloidal, slurry, and liquid phases.

- *Mixed Low-Level Waste (MLLW) /Transuranic Waste (TRU)* research advances science to solve environmental problems associated with very limited treatment options and disposal capacities.

- *Nuclear Materials* research advances science to solve environmental problems associated with unstable materials, such as plutonium metals and oxides, highly enriched uranium and nuclides of other actinide elements, and the long-term storage of stabilized materials.

- *Spent Nuclear Fuel* research advances science to solve environmental problems associated with safely and efficiently managing spent nuclear fuel from both domestic and foreign reactors.

- *Subsurface Contamination* research can assist the Department in solving environmental problems associated with hazardous and radioactive contaminants in soil and groundwater that exist throughout the DOE complex, including radionuclides, heavy metals, and dense, nonaqueous phase liquids.

- *Health, Ecology, and Risk* is a crosscutting problem area; therefore, the research investment will impact cleanup work across the Department of Energy (DOE) complex. There is scientific uncertainty about the levels of risk to human health and the environment at the end stages of the DOE cleanup effort. Accurate risk analyses require thorough knowledge of contaminant characteristics, basic ecological processes and principles, rates at which contaminants move through ecosystems, and health and ecological effects. In particular, better knowledge of radionuclide and toxic chemical transport dynamics and the potential effects of long-term exposure to low levels of radionuclides, in combination with other contaminants, is needed to assist the DOE in its efforts to protect the public, workers, and the environment. This research would also improve the understanding of threatened and damaged ecosystems and processes to restore their viability and quality.

- *Long-Term Stewardship* research supports issues that impact the Department in assessing site conditions after a site is closed and a remedy has been implemented. Long-term stewardship research is necessary to support the Department's commitment to protect human health and the environment after site closure for sites where cleanup to levels acceptable for unrestricted use is not possible.

## *Science Categories*

EMSP research is classified further within each problem area based upon the type of science being conducted. Science classifications include the following:

- Actinide Chemistry including uranium, americium, and plutonium
- Analytical Chemistry and Instrumentation includes sensor development and diagnostics such as non-destructive examination

- Biogeochemistry studies such as oxidation/reduction and biological degradation
- Engineering Science research such as robotics and remote sensing
- Geochemistry that focuses on reactions within the subsurface
- Geophysics that included advanced characterization methods
- Health Science research on dose assessment, bio-markers, and risk estimates
- Hydrogeology that targets subsurface transport mechanisms and predictive modeling
- Inorganic Chemistry including tank waste speciation and metals remediation
- Low Dose Radiation to understand the health effects of low doses of radiation
- Materials Science which studies phenomena such as corrosion, glasses and other waste forms
- Microbial Science research on areas such as bio-remediation and microbial transport
- Plant Science area such as phytoremediation
- Separations Chemistry that focuses on high level tank waste treatment alternatives.

## DOCUMENT LAYOUT FOR VOLUME 1

Research transition activities are addressed in three accomplishments categories: collaborations, research transfers, and student research. In addition, this volume contains sections covering success posters, fact sheets, and workshops sponsored by the EMSP. Communications products are documented in Volume 2.

1. *Success Posters.* These highlight several projects that are examples of EMSP research being integrated into EM cleanup. Some of these projects have been deployed at DOE sites to support cleanup while others are still in the maturation process but are closely linked to site needs.

2. *Fact Sheets.* These are summaries of EMSP projects or groups of projects linked to specific problem areas within EM. The fact sheets highlight program efforts to support EM cleanup.

3. *Collaborations.* This section reports the collaborative effort being undertaken by EMSP projects to further research and to transfer research towards technical maturity. To date, 159 collaborations have been reported.

4. *Research Transfers.* The main objective of EMSP-funded research is to address EM clean-up needs through 2070. This section highlights 32 research transfers (i.e., deployments, products, spin-off business, field tests, continuation by others, etc.) by project. Some activities listed in this section may be planned actions and are provided to ensure follow-up contacts are made.

5. *Graduate Students.* One of the two main objectives of the EMSP is to develop a cadre of environmental scientists to meet 21st century clean-up needs. This

section tracks the impact the EMSP is having on increasing the cadre of environmental researchers. The number of Post Doctoral, PhD, Masters, and Undergraduate students are reported by EMSP project. Graduate student researcher's names are noted where provided. As of March 30, 2001, 525 undergraduate, graduate, and post graduate researchers are funded under this program.

6. *TopicalWorkshops.* This is an overview of the various workshops sponsored by the EMSP to promote research integration and transfer. This includes the EMSP National Workshops, site-specific workshops focusing on a specific site such as the one hosted by the Idaho National Engineering and Environmental Laboratory (INEEL), and topical workshops such as the vadose zone series of workshops held at Hanford or the long term monitoring workshop held at INEEL.

EMSP-funded research activities are listed within each section by EMSP Problem Area and Science Category, and include the project number, title, name of the principal investigator, and a brief description of the respective project. Transitions between Problem Areas are indicated by oversized, bold text on a shaded background, with associated science categories appearing as bold text preceded by a shaded horizontal rule, as follows.

## EMSP Problem Area

### EMSP Science Category

Photos and illustrations are placed throughout the document to coincide with information regarding the EMSP research project to which they apply.

## *Success Posters*

## *SUCCESS POSTERS*

Success Posters address a problem area wherein a suite of technologies provides a solution to the problem, but are sometimes used for technology solution topics. This section includes seven Success Posters created by the EMSP to support National Workshops and various other presentations nationwide.

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# Science Advancing Solutions

*for Deactivation and Decommissioning*

## Metal Ion Analysis Using Near-infrared Dyes and the "Laboratory-on-a-Chip"


**Principal Investigator:**
Greg Collins
Naval Research Lab


**Project Number:**
64982

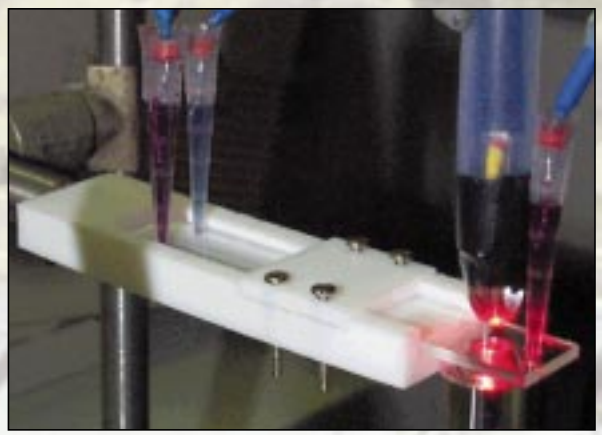
**Science Category:**
Analytical Chemistry & Instrumentation

**Value to EM Cleanup:**

- Quantification and identification of radionuclides and heavy metals, e.g., U, Pu, Cs, Sr, Hg, and Pb.
- Field portable for in-situ characterization.
- Rapid separation times, e.g., uranium characterized in less than a minute.
- Low volumes of secondary waste
- Low equipment cost.
- Low analysis cost

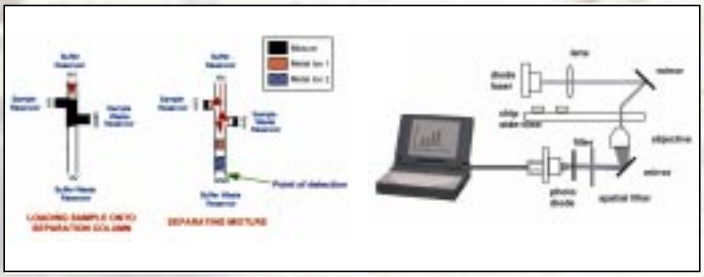
**Accomplishments:**

- Synthesis and purification of four, new fluorescence-tagged metal complexation ligands-cyclen, crown ether, iminodiacetic acid, and calix[6]arene.
- Demonstrated separation and quantitation of uranium on a microchip in less than a minute.
- Highly selective ligands or matrix components have been established for uranium detection
- Both absorbance and fluorescence detection modes have been demonstrated as sensitive modes of operation (ppb level detection limits) for uranium on a microchip.



**Voltage is applied to the four reservoirs to transport ions and liquid down the microchannels.**

**Lab-on-a-chip showing microchannels and reservoirs**



**Through a process of electroosmosis and careful selection of applied voltages, metal on complexes are separated and identified by their differences in migration.**

**EMSP**

**For additional information visit the EMSP Website at**
**http://emsp.em.doe.gov**

**Environmental Management Science Program**

# Science Advancing Solutions

*for Subsurface Contamination*

## Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media

**Principal Investigator:**
Frederick Colwell,
Idaho National Engineering and Environmental Laboratory

**Project Number:**
55416

**Science Category:**
Microbial Science

**Value to EM Cleanup:**

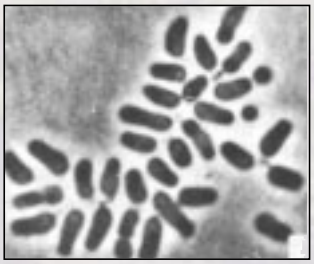
- The multi-level sampler provides an understanding of the chemical and microbiological conditions at specific vertical locations in the subsurface.
- A better understanding of subsurface chemical and microbial conditions helps identify potential in situ treatment solutions, and verify treatment effectiveness.
- Provides a necessary tool for evaluation of natural attenuation as a treatment alternative.

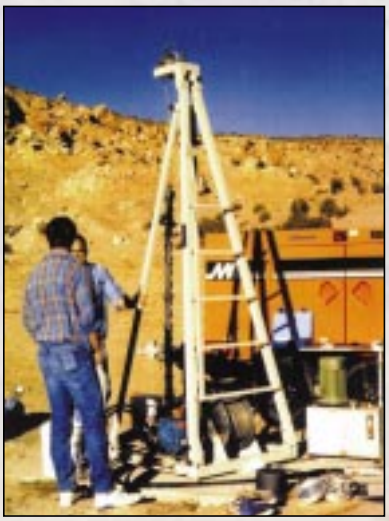
**Accomplishments:**

- Performed aseptic subsurface sampling in support of Test Area North (TAN) cleanup activities at the INEEL. Information used to establish protocols for enhanced in situ bioremediation.
- Determined the broad distribution of naturally occurring TCE-degrading microorganisms in the larger dissolved phase contaminant plume at TAN.
- Verified the presence of dissolved methane, a nutrient needed to sustain TCE-degrading microbes, in the Snake River Plain Aquifer at TAN, thus supporting a natural attenuation alternative in the proposed Record of Decision.

**Aseptic sampling of fractured rock**

**Naturally-occurring TCE-degrading microorganisms may naturally attenuate the TAN TCE plume at low concentrations**





**Understanding the chemical and microbial conditions in the subsurface helps identify potential treatment solutions**

**EMSP** For additional information visit the EMSP Website at http://emsp.em.doe.gov

**Environmental Management Science Program**

# Science Advancing Solutions

## *for Subsurface Contamination*

## Design and Development of a New Hybrid Spectroelectrochemical Sensor


**Co-Investigators:**

William R. Heineman,
Carl. J. Seliskar,
Thomas H. Ridgway,
University of Cincinnati

Samuel A. Bryan,
Timothy L. Hubler,
Pacific Northwest National Laboratory


**Project Number:**
70010

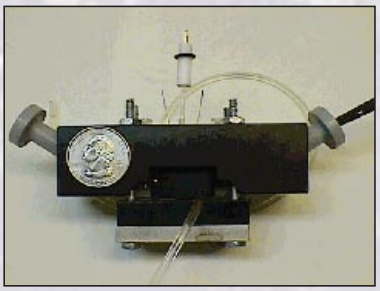
**Science Category:**
Analytical Chemistry and Instrumentation

**Value to EM**

- Aid in the characterization of complex waste material associated with DOE site cleanup
- On-site monitoring of collected and prepared samples for field evaluation
- Enhanced selectivity over currently available conventional sensors
- Monitoring of subsurface water and vadose zone

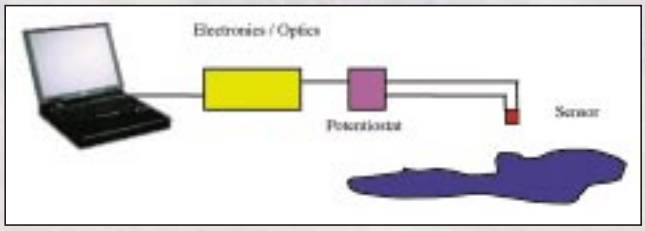
**Accomplishments**

- Concept demonstrated with detection of ferrocyanide, $Re(DMPE)_3^+$, $Ru(bipy)_3^{2+}$, and methyl viologen
- Selectivity against direct interferences demonstrated
- Signal averaging to achieve lower detection limits demonstrated
- Prototype instrumentation package to control electrochemical modulation and optical readout developed
- Sensor for detection of ferrocyanide in Hanford U-Plant 2 simulant solution demonstrated
- Sensor package (microcell and instrumentation) for demonstration on ferrocyanide in waste tank sample at Hanford developed
- This sensor has been successfully tested on technecium at concentrations ranging from 1-1,000ppm and has the possibility of being modified to detect other groundwater contaminants



**This prototype sensor has a sample volume of 800 µl. The blue LED provides a simple light source and the working electrode consists of an indium tin oxide slide coated with a charge selective film.**

**The Virtual Software interface for spectro-electrochemical sensor allows for remote control of sensors and remote monitoring of sensor response.**




**Remote sensing can be achieved with the use of a portable computer connected to the cell through a module housing the electronics for data acquisition.**

# Science Advancing Solutions

*for Deactivation and Decommissioning*

## TRU Decontamination with Plasma Etching

**Principal Investigator:**
Dr. Robert F. Hicks,
UCLA

**Project Number:**
54914

**Science Category:**
Materials Science

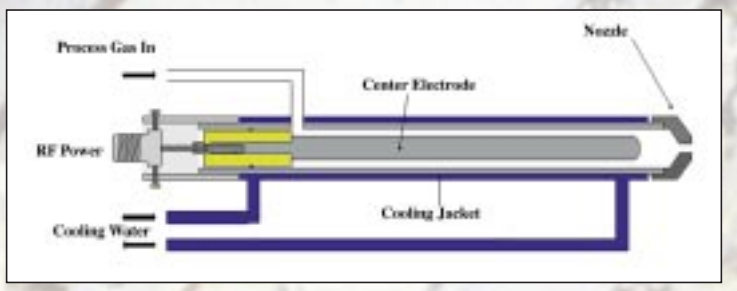
**Value to EM Cleanup:**

- Decontamination of TRU contaminated waste
- Low-pressure Low-temperature operation
- Cleaning rate of 1/2 $ft^2$/minute
- Low operating cost <$5/$ft^2$
- Low capital equipment cost <$100K
- No secondary waste
- Field Mobile

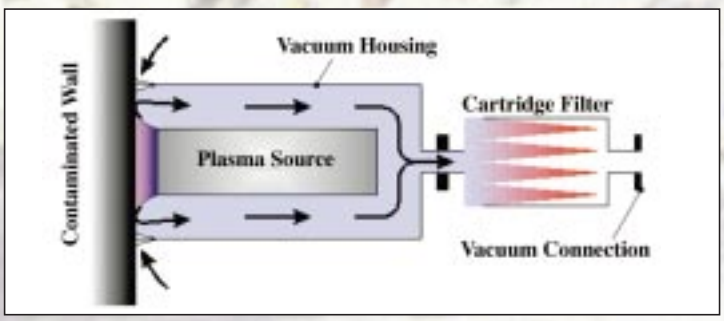
**Accomplishments:**

- We have demonstrated removal rates of tantalum, a surrogate for plutonium, in excess of 6.0µ/min.
- Vast improvements in the operability and reliability of the plasma source have been made.
- We have scaled up the source from a reactive beam area of 1.0 $cm^2$ to over 1.0 $ft^2$
- We have characterized the physics and chemistry of the atmospheric-pressure plasma jet: it generates $10^{11}cm^{-3}$ of ions and $10^{15}cm^{-3}$ of reactive neutral species.
- We have identified the surface chemistry of heavy metal etching: the rate is controlled by surface reactions between adsorbed F atoms and a metal fluoride layer.

**4" wide decontamination nozzle**




**Schematic of Atmospheric-Pressure Plasma Decontamination Technology**




**Conceptual of TRU contaminant collection system**

**EMSP** For additional information visit the EMSP Website at http://emsp.em.doe.gov

**Environmental Management Science Program**

# Science Advancing Solutions

## *for Subsurface Contamination*

## High Resolution Definition of Subsurface Heterogeneity for Understanding the Biodynamics of Natural Field Systems: Advancing the Ability for Scaling to Field Conditions

**Principal Investigator:**
Dr. Ernest L. Majer,
Lawrence Berkeley National Laboratory

**Project Number:**
55264

**Science Category:**
Microbial Transport

**Value to EM Cleanup:**

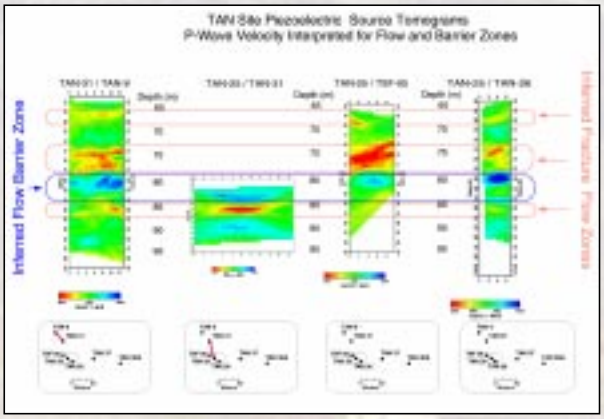
- Provides a cost-effective method for delineating the volume and distribution of highly contaminated fracture zones.
- Can be used to focus remediation efforts, estimate the duration of the remediation effort and to modify the conceptual model for implementing restoration at contaminated sites.

**Accomplishments:**

- Seismic Crosshole Tomography was successfully employed to image the subsurface between several ground water extraction and monitoring wells at the INEEL Test Area North (TAN)
- Low velocity zones delineated by seismic tomography correlate to fractured intervals known to contain elevated levels of 137Cs and 60Co.
- High velocity zones correlate to intervals of dense basalt with significantly lower concentrations of radionuclides.

**Seismic recording van and receiver well with tripod**

**Sensors being checked for contamination**




**Seismic velocity tomograms show correlation between fractured flow zones and contamination.**

**EMSP** For additional information visit the EMSP Website at http://emsp.em.doe.gov

**Environmental Management Science Program**

# Science Advancing Solutions

*for Deactivation and Decommissioning*

## D&D in Virtual Reality: A near-real-time, semi-autonomous virtualization modeling and imaging system to facilitate tele-operated D&D activities

**Principal Investigator:**
Dr. Robert J. Schalkoff,
Clemson University

**Project Number:**
55052

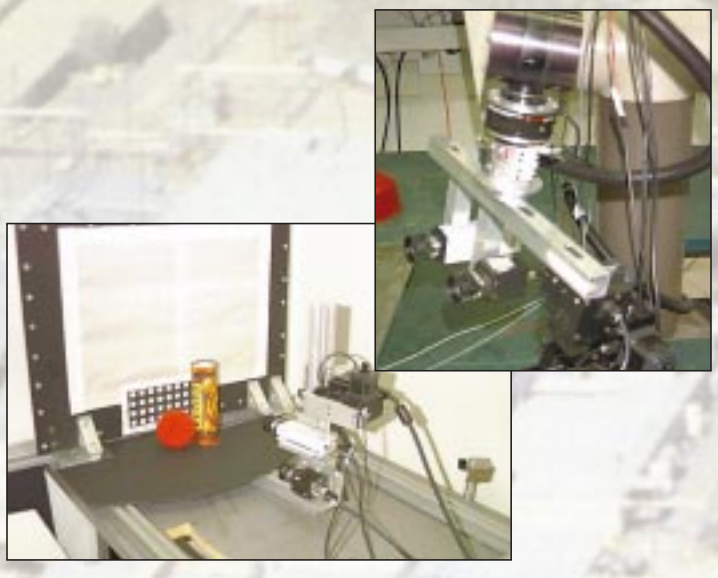
**Science Category:**
Engineering Science

**Value to EM Cleanup:**

- 3-dimensional model for Project Planning and Visualization.
- Virtual world operator training.
- Collision avoidance and tele-robotic guidance.
- Waste Packaging and handling optimization
- Reduces worker exposures in hazardous environments.

**Accomplishments:**

- A fourth generation vision sensing head has been built and tested
- The project is in the process of integrating the imaging system, the Virtual Reality rendering, and the robotics system, into a single operating unit.
- Negotiations are underway to locate a site for phase one testing of the integrated system under more realistic field conditions. The INEEL has expressed an interest in testing at their site in support of the DDROPS.
- Other parties outside the DOE have expressed interest in more refined development of the system.



Laser and camera setup during one of the initial system tests demonstrating the compact size of the scanners.

Image scanning system mounted on robotic arm for remote operations

**EMSP** For additional information visit the EMSP Website at http://emsp.em.doe.gov

**Environmental Management Science Program**

# Science Advancing Solutions

## *for Subsurface Contamination*

## Microcantilever Sensors

**Principal Investigator:**
Thomas G. Thundat
Oak Ridge National Laboratory

**Project Number:**
60197

**Science Category:**
Analytical Chemistry and Instrumentation

**Value to EM Cleanup:**

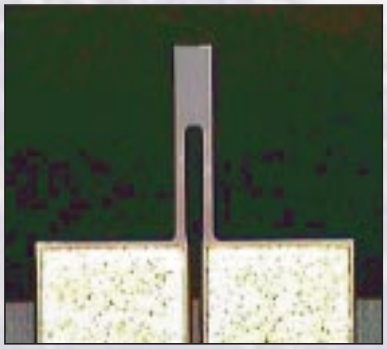
- Basis for real-time, portable, low-cost sensors for remediation and characterization.
- Single platform for chemical, physical, and radiological characterization of ground water and mixed waste.
- Identification of analytes with sub ppb sensitivity.

**Advantages:**

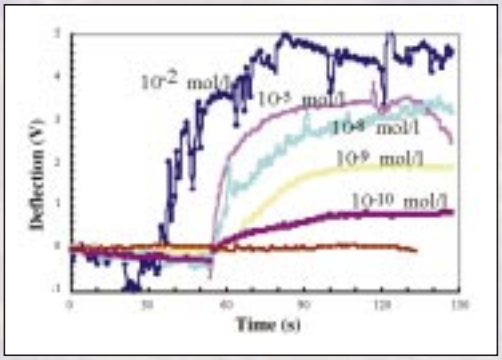
- Operates in solution.
- High sensitivity and selectivity.
- Single platform for physical, chemical, and radiological detection.
- No tagants or labeling necessary.
- Miniature and consumes less power.
- Can be micromachined and mass produced.

**Accomplishments:**

- Demonstrated detection of $Cs^+$ with $10^{-12}$M sensitivity (dynamic range $10^{-2}$ - $10^{-12}$M). Detected $CrO_4^{2-}$, Pb, $Na^+$, and $K^+$ ions.
- Detected alpha particles.
- Detected $Cs^+$ in tank waste simulant with high concentration of $Na^+$ and $K^+$ ions
- Demonstrated pH detection with high sensitivity ($10^{-3}$ pH units).
- Detection of VOCs such as benzene.

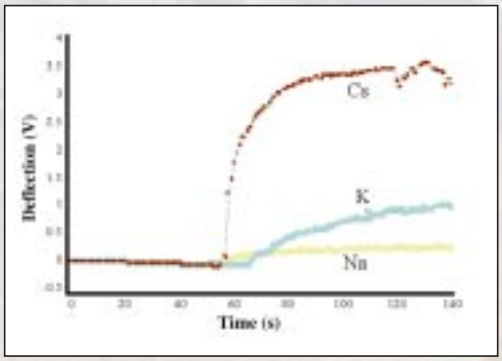


**Optical image of a 180µm long silicon mirocrocantilever.**




**Microcantilever deflection as a function of $Cs^+$ ion concentration.**

**Microcantilever bending response for $10^{-5}$M solutions of $Cs^+$, $K^+$, and $Na^+$**

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**Environmental Management Science Program**

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# *FACT SHEETS*

This section includes Fact Sheets highlighting EMSP Science Categories and associated Work Packages. These Fact Sheets were selected as part of an evaluation that focused primarily on the projects in the EMSP portfolio that were in more mature stages of development.

The Facts Sheets contained herein highlight 1997 and 1998 EMSP-funded research projects; the original release date appears in the header of each individual Fact Sheet.

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# ANALYTICAL CHEMISTRY AND INSTRUMENTATION

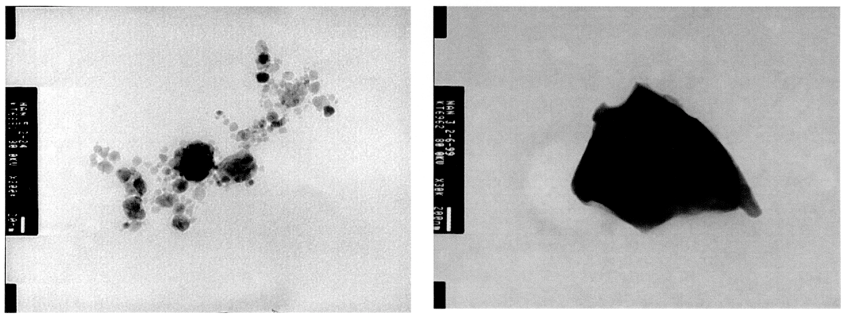
## EMSP PROJECTS APPLY WELL-KNOWN AND NOVEL ANALYTICAL METHODS AND INSTRUMENTS TO ENVIRONMENTAL MANAGEMENT PROBLEMS

Improved analytical chemistry methods and instruments are particularly important for the first and last steps of remediation. Initially, any treatment process requires a thorough characterization of the materials to be encountered during the process. Later, improved instrumentation for long-term monitoring is essential to minimize both cost and risk for long-term stewardship of closed sites.

This document describes EMSP projects that address analytical chemistry and instrumentation. Although these projects are presented by the Focus Area of most direct interest, most of the techniques and methods are applicable to a wide range of problems, as discussed below.

- Mass spectroscopy studies focus on thermospray mass spectrometry of species that have been separated by liquid chromatography, laser ablation methods for mass spectrometric analysis of solids, a new mass spectrometer for analysis of solids at high temperatures, the use of polymer membranes for introducing low-volatility organic compounds into a mass spectrometer, and a laser-induced acoustic desorption method for DNA mutation screening.
- Studies on optical methods of analysis involve fiber-optic arrays with selective fluorescence techniques, applications of cavity ringdown spectroscopy for trace analysis in the gas phase, and a new type of attenuated total reflection spectroscopy similar to cavity ringdown spectroscopy for analysis of liquids.
- Development of improved detectors of high-energy radiation targets improved continuous air monitors for alpha-particle detection, monitoring of radioactive heavy noble gas isotopes, and gamma-ray imaging and spectroscopy via a field-portable gamma-ray instrument.
- Other research involves an investigation of electrochemical methods for tank corrosion monitoring, applications of a new analytical methodology that uses microcantilever sensors, and the construction of a miniaturized version of a nuclear magnetic resonance spectrometer for analysis and process monitoring.

**TEM Images of $NaNO_3$ Particles Produced at 1064 nm, 5.0 J/cm²**



**Particle Generation by Laser Ablation**
A Washington State University project (60075) has studied characteristics of particles produced from several materials as a function of laser wavelength and power density. The goal is to improve understanding of the vaporization processes to improve the quantitative accuracy of the technique.

### PROBLEMS/SOLUTIONS

- Increasingly stringent regulatory standards demand more sensitive and accurate effluent monitoring. EMSP projects are exploring new methods such as cavity ringdown spectroscopy and microcantilever sensors as well as new applications of mass spectrometry and nuclear magnetic resonance techniques.
- Storage tanks at the Hanford site contain about 200 million curies of radioactivity and 240,000 tons of chemicals. Final closure of the tank farm is scheduled for 2032. An EMSP project is directed toward developing new methods for detecting corrosion of the tanks so that action can be taken before the tanks begin to leak.
- A recent assessment of long-term stewardship noted a strong need for better, cheaper, more reliable, and less labor intensive monitoring technology. An EMSP project is exploring development of a new technology, microcantilever sensors, as a potential solution for this long-term monitoring need.

### ANTICIPATED IMPACT

- Mass spectrometric techniques are advantageous for characterization of highly radioactive materials because they require very small samples. In this area, five EMSP projects are directed toward developing improved methods for introducing samples into a mass spectrometer so that more quantitative measurements can be made.
- An EMSP project is leading an effort to use cavity ringdown spectroscopy, an exciting new development, as a practical analytical tool with extremely high sensitivity for species of interest in DOE remediation activities.
- All major chemistry laboratories use nuclear magnetic resonance (NMR) instruments to identify and characterize organic compounds, but such instruments are typically too expensive for field use. An EMSP project is attempting to develop inexpensive, miniaturized NMR instrumentation for applications such as process monitoring in waste remediation activities, in-field characterization of waste materials, and downhole monitoring of groundwater.

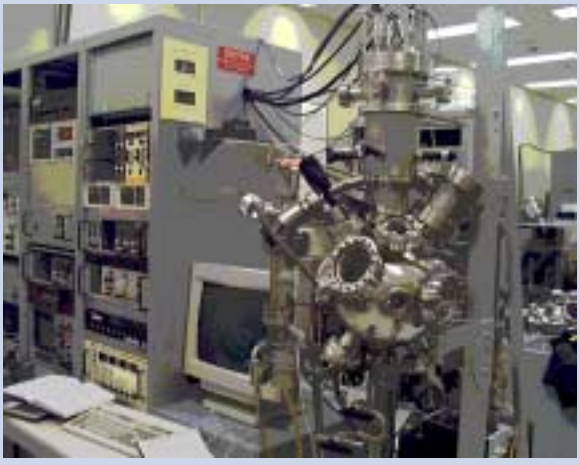
## Characterization of High-Level Tanks and Tank Wastes

*Characterization of Organic Complexants in Wastes.* The goal of the ORNL/University of Minnesota project (59978) is to enhance understanding of the equilibria for organic complexing agents and their products with metals in aqueous solutions. The university group is working on liquid chromatographic separations on zirconia-based supports, and the ORNL group is investigating the thermospray mass spectrometry of these species to aid in defining solution behavior. The objective is to combine these efforts to improve characterization of the multicomponent mixtures present in most DOE wastes containing these substances.

*Particle Generation by Laser Ablation.* Analytical techniques that minimize the amount of material needed for an analysis are particularly desirable for highly radioactive materials. One promising method uses a laser pulse to introduce a small amount of a sample into a vapor stream, which then carries it into a plasma where it is vaporized and ionized before introduction into a mass spectrometer. However, laser ablation may not volatilize a sample and a calibration standard with the same efficiency, which means that the accuracy of the determination may be inadequate. The Washington State University/PNNL project (60075) has studied the characteristics of the particles produced from several materials as a function of laser wavelength and power density. The goal is to improve understanding of the vaporization processes to improve the quantitative accuracy of the technique.

*Array Sensors for In-Situ Analysis of Tank Waste.* The objective of the ORNL/Tufts University project (60217) is to develop a selective sensor for direct determination of metal ions in a high-level tank. The project plans to prepare a series of crown ethers that preferentially bind certain metal ions with detection based on enhanced fluorescence when a metal ion is bound. A complexing agent would then be incorporated into a polymer matrix that is attached to the end of a fiber-optic cable, and a bundle of these fibers with different complexing agents would constitute the array sensor. The goal is to test an imaging fiber with an array of sensor sites selective for cesium, sodium, and potassium ions.

*Electrochemical Techniques for Monitoring Corrosion of High-Level Waste Tanks.* Corrosion of metals is an electrochemical phenomenon, and the Penn State University project (60219) has used a variety of electrochemical techniques to explore some fundamental aspects of both general and localized corrosion of iron and carbon steel in alkaline environments similar to those used for high-level waste storage at Hanford and Savannah River. Electrochemical techniques have been used for characterizations of the passive layers on iron with and without organic complexing agents present, and it was shown that the presence of EDTA caused substantial differences in the nature of the passive layer compared to EDTA-free solutions. Penn State researchers are exploring fundamental aspects of stress corrosion cracking in AISI 4340 steel (simulating a heat affected zone adjacent to a tank weld) in concentrated caustic environments. By measuring the coupling current that flows from a crack to the external surfaces, the researchers have been able to detect and characterize for the first time *individual* fracture events occurring at the crack tip. The individual fracture events give rise to a sudden increase in the coupling current (in the negative direction) followed by a slow relaxation.



**Mass Spectrometric Analysis**
This HT-SIMS instrument and electronic components were constructed by an Idaho National Engineering and Environmental Laboratory project (60424) to characterize high-temperature behavior of high-level waste forms.

*Mass Spectrometric Analysis of Solids at High Temperatures.* The INEEL project (60424) involves construction of a new mass spectrometer system that will enable analysis of materials at temperatures up to 1,750°C using electron-impact ionization of gas phase neutral species, static secondary-ion mass spectrometry (SIMS) of surface species, and dynamic SIMS for bulk species with both positive and negative ion detection. All of these analyses can be performed on the same sample, thus avoiding some of the ambiguities that result from traditional studies that use several instruments with different samples for each. The primary application of the new instrument will be to characterize the high-temperature behavior of high-level waste forms to enable more confident predictions of their stability over long times.

## Determination of Species in Mixed Wastes

*Membrane Introduction Mass Spectrometry.* A polymer membrane can be used as the interface between a liquid or gas and the vacuum in a mass spectrometer. The most common application of this technique is with membranes that preferentially transport volatile organic compounds through the membrane for subsequent analysis by mass spectroscopy.

The goal of a LANL project (59981) is to extend this technique to include less volatile organic and organometallic compounds to enable characterization of mixed wastes and incinerator effluents. Chemical ionization of analytes using ions derived from oxygen or water has been found preferable to other ionization methods, and simultaneous detection of volatile, semivolatile, and organometallic compounds in air and water has been demonstrated with this ionization technique. Several types of membranes have been explored to enable more selective determinations of more polar and less volatile analytes.

*Cavity Ringdown Spectroscopy.* If a tunable laser pulse is introduced into the space between two highly reflective mirrors, then the pulse will be reflected back and forth in the cavity. The intensity of the beam will be slightly decreased on each transit due to reflectivity losses at the mirrors, light scattering by the air in the cavity, and absorption by one or more gases in the cavity. Cavity ringdown spectroscopy (CRDS) involves measuring the rate of decay of the light intensity in the cavity as a function of the wavelength of the laser pulse. A Mississippi State University project (60070) was conducted to provide the first quantitative evaluation of CRDS for trace analysis using inductively coupled plasma (ICP), graphite furnace, and cold vapor methods for introducing an absorbing analyte into the cavity. Early studies showed a detection limit for mercury of 20 parts per billion with an ICP method, as compared to a potential limit of 0.2 ppb. Detection limits for determinations of lead and mercury using graphite furnace atomization were found to be at least three times lower than those obtained by conventional atomic absorption methods. A CRDS determination of mercury using a cold vapor method had a detection limit of 25 nanograms per cubic meter, which was more than 300 times lower than that achieved with conventional atomic absorption methods.

*Miniature Spectrometer for Remote Chemical Detection.* Light that is incident at certain angles on the interface between high and low index of refraction media can be totally reflected. A substance on the surface will result in an attenuation of total reflection (ATR) at wavelengths where the substance absorbs light, and this ATR technique has been widely used, particularly in infrared spectroscopy. The NIST project (60231) has involved a new type of ATR spectroscopy that is similar to the CRDS described above. If a light pulse is introduced into a solid such that it is internally reflected at successive surfaces and thus travels in a ring, then the ATR phenomenon at one of the surfaces will result in a "ringdown" time that is shortened. Various crystals may be used to form the ring cavities, and along with optical fibers can be used to produce a miniature spectrometer for remote spectroscopic measurements on substances in contact with the crystal. This work has resulted in several patents for a new method for high sensitivity measurements of optical properties of materials.

### Project Teams

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  PI: Philip H. Hemberger (59981)
- Mississippi State University
  PI: George P. Miller (60070)
- Washington State University
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  Pacific Northwest National Laboratory
- Naval Research Laboratory
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  Lawrence Berkeley National Laboratory
- New Mexico Institute of Mining & Technology
  PI: Stephen D. Schery (60163)
  Los Alamos National Laboratory
- Oak Ridge National Laboratory
  PI: Thomas G. Thundat (60197)
- Oak Ridge National Laboratory
  PI: Gilbert M. Brown (60217)
  Tufts University
- Oak Ridge National Laboratory
  PI: Chung Hsuan Chen (60218)
- Pennsylvania State University
  PI: Digby D. MacDonald (60219)
- National Institute of Standards & Technology, Gaithersburg
  PI: Andrew C. R. Pipino (60231)
- University of Illinois–Chicago
  PI: Gennady Friedman (60247)
- Idaho National Engineering & Environmental Laboratory
  PI: James E. Delmore (60424)
- Georgia Institute of Technology
  PI: John D. Valentine (60474)
  Argonne National Laboratory

## Monitors for Health Risk Evaluation or Assessment

*Applications of Alpha, Beta, and Gamma Ray Detectors.* The New Mexico Tech/LANL project (60163) is studying environmental influences that can cause degradation of the performance of continuous air monitors (CAMs), such as those used for alpha-particle detection. The monitors are frequently located in dusty environments, and part of this study has been directed toward understanding the ambient aerosol particulate deposits on CAM filters and the effect of these deposits on the monitor's performance. They have studied how the pattern of particles on a filter influences resolution of alpha spectra by the monitor. A measurement of the aerosol size distribution at the Waste Isolation Pilot Plant was conducted to ensure that the laboratory studies were relevant to actual field conditions.

*Mass Spectrometry Mutation Screening for Contaminant Impact Analysis.* An ability to perform rapid mutation screening is an essential part of contaminant risk analysis, but rapid, reliable DNA mutation screening is still not available. An ORNL project (60218) is exploring some innovative mass spectrometry techniques for possible

application to this important problem. This group has designed and tested a laser-induced acoustic desorption facility with resulting mass resolution better than that obtained with conventional methods. The percentage of cells with mutant DNA caused by a contaminant is very small, thus techniques for amplification of a mutant are being used prior to the mass spectrometric detection. Direct sequencing of DNA primers and probes remains a significant challenge. Even though this project has not yet developed a complete analytical system for rapid screening, the advances in mass-spectrometric techniques for large molecules are important steps toward achieving the goal.

*Detectors for Radioactive Noble Gases.* The primary objective of a Georgia Tech/ANL project (60474) is to develop better detectors for some of the radioactive heavy noble gas isotopes. Projected applications include long-term monitoring of uranium, thorium, and transuranic wastes as well as alpha particle air monitors that discriminate between radon emissions and other alpha emitters. The first stage of the monitor will rely on a fluid transfer process in which heavy noble gases in the atmosphere are preferentially absorbed by certain organic fluids and subsequently degassed before detection. The best system sensitivity results from a detection scheme that distinguishes between alpha and beta particles in addition to recording gamma-ray spectra. The team has found that sophisticated beta/gamma coincidence detection techniques result in higher sensitivity with lower background counts. A pulse processing system that allows dual-parameter pulse height analyses of coincidence events provides a superior ability to distinguish the different isotopes. The final result is intended to be fieldable systems consisting of a fluid transfer system and an optimized detection system.

## Characterization of Spent Fuel

*Field Portable Instrument for Gamma-Ray Imaging and Spectroscopy.* The goal of a Naval Research Laboratory/LBNL project (60141) is to develop field-portable gamma-ray detectors that can both image gamma rays from radioactive emitters and determine the isotopic composition by using gamma spectroscopy. The project consists of developing an array of double-sided germanium strip detectors. A prototype system was developed using existing germanium detector technology. A double-sided orthogonal strip germanium detector was fabricated for the first time with an amorphous contact process for the purpose of improving imaging capabilities. The image capabilities of the system will be tested with simple uranium and thorium pieces, and then field tests will be conducted with plutonium buttons and spent fuel rods.

## New Analytical Tools for Subsurface Contaminants, Mixed Wastes, and Tank Wastes

*Microcantilever Sensors.* An ORNL project (60197) has been exploring the use of microcantilever sensors for real-time, in-situ chemical, physical, and radiological sensors. The silicon-based microcantilevers are similar to those used for atomic force microscopy. Changes in cantilever position or vibration frequency can be detected by using reflected laser light. By attaching selective coatings onto the cantilevers, the sensors can be made highly selective. For example, by coating the cantilevers with cesium-selective ionophores, cesium ions could be detected at concentrations as low as $10^{-12}$ molar. Modified cantilevers for selective determinations of lead, mercury, chromium, and strontium in groundwater were also being developed. Other applications include highly sensitive sensors for changes in pH, sensors for benzene, toluene, and hydrogen, and a novel detector for alpha particles.

*Nuclear Magnetic Resonance.* All major chemistry laboratories use nuclear magnetic resonance (NMR) instruments to identify known chemical species and to elucidate the structures of new compounds. However, high-resolution instruments can cost several hundred thousand dollars and are not suitable for use as process monitors or for in-field characterization of waste materials. The objective of a University of Illinois–Chicago project (60247) is to design and build a highly miniaturized version of a NMR spectrometer for in-situ and in-process analysis and monitoring. The group has published several papers that describe the theoretical and experimental studies that have been used to explore the best techniques for constructing a system with a permanent magnet that would be small enough to be held in the palm of a hand. The initial instrument will be designed for doing proton NMR, but extensions to fluorine, phosphorous-31, and carbon-13 are projected. Planned applications include downhole monitoring of groundwater, in-process monitoring of remediation activities, compositional analysis of chemicals in storage tanks, and in-field characterization of waste materials.

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# ENGINEERING SCIENCE

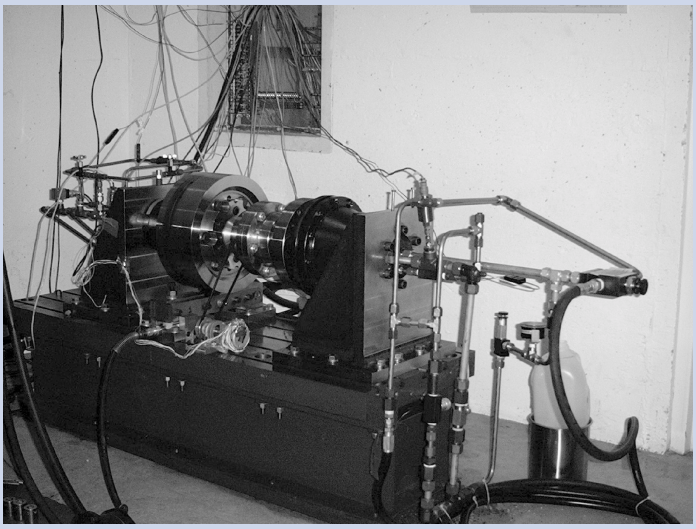
## Basic research in engineering science provides the basis for more efficient practical problems

Engineering science projects in support of the Deactivation and Decommissioning Focus Area include a project designed to develop methods to detect impending failures of robots before they can damage containment facilities or cause mission failures. Another project demonstrated the effectiveness of a pulsed laser system for the removal of contaminants from concrete surfaces.

Another EMSP project is targeting improvement of the basic understanding of the causes of formation of foams in sludges and slurries in high-level waste tanks and use of this understanding to develop improved antifoaming agents. In another study, work is directed toward improved understanding of the behavior of bubbles of the flammable gases formed by radiolysis processes in high-level waste tanks so that safety hazards caused by these gases can be minimized.

To enable more reliable design of engineering operations, such as separations, for the complex materials in mixed wastes, one EMSP project is performing both experimental and modeling studies. Another project is exploring potential processes for reducing the volume of mixed wastes by using high-temperatures to destroy the organic compounds while using sorbents to capture volatilized metals.

In another engineering project, researchers are doing fundamental modeling work that uses new computational and analytical methods to improve criticality safety assessments associated with fissile material processing. These methods will also be tested for application to nuclear fuel storage problems. Another study has been directed toward fundamental studies of fluid flow in systems in which exothermic reactions occur with one or more components of the fluid. The objective is to gain a more thorough understanding of the methods used to prevent pyrophoric reactions of air with spent nuclear fuel when it is removed from storage under water.



**Early Detection of Impending Failure in Robots**
This test rig was built by a Foster-Miller Technologies project (60040) to evaluate diagnostic methods and applicability to hydraulic robots.

### Problems/Solutions

- Undetected faults in the robots to be used at many DOE sites could have serious consequences, including damage to waste containment facilities or delays in remediation because of robot failure. An EMSP project is addressing methods for early detection of impending failure in the hydraulic robot systems likely to be used in DOE applications.
- The formation of foams can seriously impede operations with high-level waste. For example, during a recent continuous precipitation removal test at Savannah River, formation of foam caused the premature termination of one test and the interruption of a second test. A fundamental study of foam formation has led to development of a new antifoaming agent that is particularly useful for high-temperature operations.

### Anticipated Impact

- Flammable gases are formed in high-level waste tanks due to radiolysis of tank materials. Changes in the volume of tank contents with atmospheric pressure changes may provide a method to determine the total volume of gas bubbles present in the tank waste and thus avoid expensive direct determinations.
- A state-of-the-art apparatus is being used in an EMSP project to measure thermodynamic properties of complex mixed waste systems. These studies will form the basis for designing separation processes for which no design data have previously been available.
- A thorough understanding of the physical phenomena related to criticality safety issues is essential to optimize fissile material operations. A major EMSP project is directed toward developing nuclear analysis capabilities for waste management activities.
- A study of flow visualization will allow determination of optimal geometries for spent nuclear fuel in a drying chamber and verification that the exposed fuel will not undergo rapid reactions when exposed to air.

# Technical Summary and Progress

## Early Detection of Impending Failure in Robots

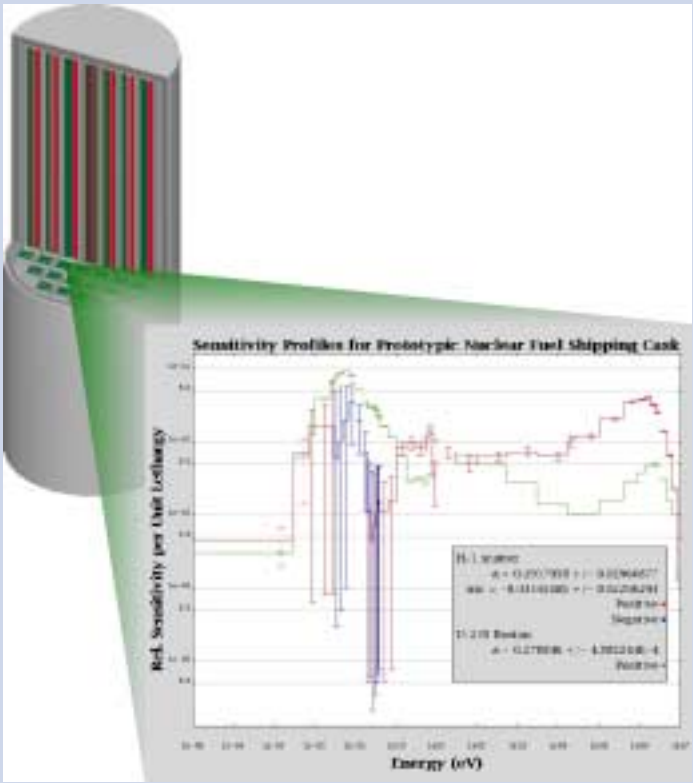
Deactivation and decommissioning of many hazardous waste sites in the DOE complex will require use of robots, and thus a number of robotic systems have been developed in DOE-funded work. For example, a hydraulic robot system has been developed to deploy tooling for equipment removal and other D&D tasks (see TMS Tech ID #1799 at http://ost.em.doe.gov/tms/Home/Entry.asp). A Foster-Miller Technologies/Rice University project (60040) was undertaken to develop monitoring and diagnostic methods for robots that would enable early detection, isolation, and tracking of impending faults before they result in robot failure. Such methods have not previously proven effective for hydraulic robots.

## Laser Ablation of Concrete Surfaces

An ANL project (60283) has shown that an industrial 1600-watt Nd:YAG laser operated in the near infrared efficiently removed a 1-mm by 3-mm deep section of concrete on each pass. The work has shown that a pulsed laser ablation system is scalable and robust and that it is preferable to continuous laser systems. Because of fiber-optic beam delivery, the laser can be far removed from the surface, and the only moving part is the focusing head, which is inexpensive and can be moved easily with a robot arm. Under appropriate conditions most of the effluent consists of powder along with a small amount of aerosol. The amount of aerosol is enhanced as melting increases and efficiency drops. Detailed studies of composition as a function of aerosol particle size showed that the smallest aerosol particles were enriched in cesium, whereas the intermediate size particles were enriched in strontium. Thus, the project has shown that a laser ablation system can be used for cleaning of concrete surfaces provided that due care is taken to capture the aerosol particles.

## Foams and Bubbles in High-Level Waste Tanks

The objective of an Illinois Institute of Technology project (60143) is to develop a basic understanding of the mechanisms that produce foams in solid-liquid-gas systems. Instrumental techniques being employed include differential microinterferometry, film rheometry, and a capillary force balance. Studies of the formation of foams in the presence of simulated sludge or silica have shown that foaminess increases to a maximum when particle concentration is increased. The amount of foaminess decreases exponentially with increasing particle size for a given concentration of solids. Effects of the presence of electrolytes and other inorganic and organic substances in the tanks on foam formation are also being investigated. Based on the knowledge of the origins of foam formation developed in this study, an improved antifoaming agent was developed and tested in both laboratory-scale and pilot-scale experiments at the Savannah River Site.




**Nuclear Criticality Safety Analyses for Nuclear Materials**
An Oak Ridge National Laboratory project (60077) has been developing more reliable computational techniques for nuclear criticality safety analyses.

The Hanford tanks contain some flammable gases (hydrogen, ammonia, and nitrous oxide) that form bubbles that are trapped in the sludges and slurries in the tanks. The objective of a PNNL/LBNL/University of Texas project (60451) is to gain a fundamental understanding of the interactions of the bubbles and tank waste during barometric pressure fluctuations in order to anticipate flammable gas safety hazards associated with future waste operations. The project involves an experimental study of bubbles in continuum materials and in particulates, both solid mechanics and fluid mechanics modeling of bubbles in continuum materials, and modeling of bubbles in particulate materials. Both the experimental and modeling studies are developing an understanding of the observed hysteresis in the change in tank level with changes in pressure, and experiments to resolve the remaining ambiguities have been suggested.

## Physical and Chemical Properties of Mixed Waste

Some of the mixed waste inventory at DOE sites is aqueous waste, and knowledge of the basic thermophysical properties of these complex systems is needed to aid in the design of treatment and disposal processes. The objectives of the NIST/Michigan Technological University project (60155) are (1) to develop and validate models that predict the phase equilibria and thermodynamic

properties of hazardous aqueous systems and (2) to measure the thermodynamic properties of a representative system that contains water, acetone, isopropyl alcohol, and sodium nitrate. The models have been used to predict the vapor pressure and vapor composition as a function of temperature and liquid composition for pure solvents, solvent mixtures, and mixtures that also contain salts. The experimental measurements are being done using an ebulliometer at Michigan Tech, a high-temperature/high-pressure phase equilibria apparatus at NIST, and a coexisting density and vapor-liquid equilibrium apparatus at NIST.

Mixed wastes contain both radioactive and other hazardous materials, which are usually organic compounds. One potential process for reducing the volume of these wastes is to use high temperatures to destroy the organic compounds and capture volatilized metals by sorbents. The objective of the University of Arizona/University of Illinois/EPA/SNL project (60326) is to provide the background information necessary to design such a process using hot turbulent flows. They have shown that cesium and strontium can be captured on substrates after injection into turbulent flames, and a laser diagnostic system is being installed to enable in-situ measurements of solid, droplet, and vapor metal species. A key part of their effort has been to develop reliable models for metal-containing liquid droplets going through a highly turbulent combustor.

### Project Teams

**Lead Principal Investigator (Award Number)**

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  Rice University
- Oak Ridge National Laboratory
  PI: Cecil V. Parks (60077)
- Illinois Institute of Technology
  PI: Darsh T. Wasan (60143)
- University of Idaho
  PI: John C. Crepeau (60144)
  Clarksean and Associates
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  Michigan Technological University
- Argonne National Laboratory
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- University of Arizona
  PI: Jost O. L. Wendt (60326)
  University of Illinois
  EPA National Risk Management Research Laboratory
  Sandia National Laboratory–California
- Pacific Northwest National Laboratory
  PI: Phillip A Gauglitz (60451)
  Lawrence Berkeley National Laboratory
  University of Texas–Austin

### Nuclear Criticality Safety Analyses for Nuclear Materials

An ORNL project (60077) has been directed toward development of more reliable computational techniques for nuclear criticality safety analyses. New techniques have been developed for the calculation of the sensitivity coefficients of the system's neutron multiplication to perturbations in the cross section data using Monte Carlo calculations. Applications of the codes have been made to systems with thermal, intermediate, and fast neutron spectra, mixed-oxide and uranium-fueled systems, and a variety of geometries ranging from simple spheres to large arrays of fuel rods. The methods developed through this project will allow improved characterization of the complicated, heterogeneous fuel assemblies typical of the spent fuel inventory.

### Visualization of Flow in Spent Nuclear Fuel Passivation Operations

Extended underwater storage of spent nuclear fuel elements can result in the formation of uranium hydride in corroded areas of the elements. When the elements are removed from water storage and exposed to air, the uranium hydride can react very rapidly with the oxygen in air. By passing an inert gas containing a small amount of oxygen over the fuel elements, they can be passivated by slowly forming oxide layers. The goal of the University of Idaho/Clarksean/INEEL/Ohio State University project (60144) was to develop flow visualization methods and reliable predictive techniques for the energy, mass, and momentum transfer in the presence of surface reactions that occur during passivation treatment operations. They have developed an experimental apparatus to simulate reactive flow patterns and have shown that reactions may decrease the likelihood that all corroded areas will be properly treated. Other experiments have been used to obtain fundamental measurements of the velocity and turbulence fields in idealizations of fuel canisters. Various turbulence models were used to model the pipe flow in support of the experimental work.


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**Office of Environmental Management**
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# GEOCHEMISTRY AND BIOGEOCHEMISTRY

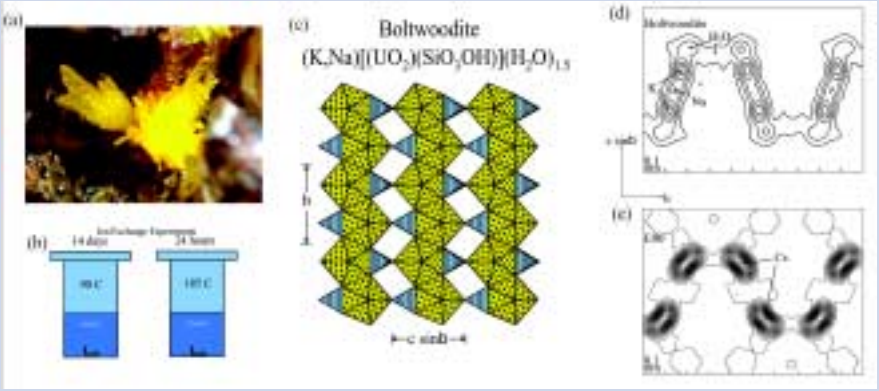
## Long-term risk assessment requires a thorough understanding of the interactions between hazardous materials and minerals in the subsurface

The most prudent action in regard to a radioisotope in a chemical form that is tightly bound to components in the subsurface may be to take no remedial action because radioactive decay to less hazardous forms may occur before the hazardous material has migrated from the original site. Thus, a thorough understanding of the mobility of hazardous materials in the subsurface is crucial to risk assessments and to designing remedial action for subsurface contaminants. In response to this need, several DOE EMSP projects are targeting advanced understanding in this area.

In regard to repository use, which is of prime interest to the National Spent Fuel Program, regulators require a sound technical basis for predictions of the long-term behavior of stored fuel. Two closely related EMSP projects are investigating the chemistry of uranium oxides under the oxidizing conditions anticipated for the Yucca Mountain repository to determine whether migration of hazardous components of the fuel will be enhanced or retarded.

Plutonium mobility is a high visibility issue at Rocky Flats and Hanford, and the mobility of actinides is a key concern at several other DOE facilities. An EMSP project is designed to delineate the methods by which actinides in surface soils are mobilized under various conditions so that reliable risk assessments can be made.

Another project has studied the chemistry of residual sludge components to determine whether it will be necessary to remove all sludge heels from waste tanks before grouting and final closure. Some Hanford tanks have already leaked nearly a million gallons of water, and one EMSP project has been assessing whether remedial action is necessary to prevent migration of the radioactive cesium that has leaked into the subsurface.




**Consequences of Corrosion of Spent Nuclear Fuel in a Repository**
These images from a Notre Dame project (59960) depict ion exchange of Cs and K and Na in Boltwoodite using a 2M CsCl solution: (a) crystals of Boltwoodite, (b) experiment design, (c) uranyl silicate sheet in Boltwoodite, (d) electron density in the interlayer of an untreated crystal obtained from X-ray diffraction, (e) electron density in the interlayer of the crystal treated at 90°C obtained from X-ray diffraction. Contour intervals are identical in (d) and (e).

### Problems/Solutions

- Removing all of the sludge from the walls of high-level storage tanks before closure by filling the tank with grout would be extremely difficult and expensive; however, the risks associated with leaving the sludge heels in the tank must be understood. An EMSP project has been designed to quantify radioactive release rates from these sludges if grouted tanks are exposed to groundwater.
- Before spent nuclear fuel can be sent to a permanent repository, DOE must show that the repository system can safely isolate fuel from the environment. Two EMSP projects are investigating the chemistry of uranium oxides under repository conditions in order to contribute fundamental data necessary for the National Spent Nuclear Fuel Program to perform a total system performance assessment.

### Anticipated Impact

- Deep cesium-137 migration beneath Hanford tanks that have leaked has resulted in significant regulatory and stakeholder concerns. An EMSP project is designed to determine whether cesium will be sufficiently bound to subsurface minerals to retard migration long enough for radioactive decay to occur to levels that do not pose a substantial danger to the environment. If so, then expensive efforts to recover the cesium can be avoided.
- The mobility of actinides in surface soils at DOE facilities in dry climates is a major source of risk to human health and the environment. The means by which actinides in surface soils migrate in dry climates has been studied in detail by an EMSP project in an effort to improve risk assessments and guide remediation efforts.

# Technical Summary and Progress

## Consequences of Corrosion of Spent Nuclear Fuel in a Repository

In an oxidizing environment such as that in the proposed repository at Yucca Mountain, the uranium dioxide in spent nuclear fuel may be rapidly converted to uranyl compounds that are often highly soluble. A University of Michigan project (59849) is designed to identify reaction paths that form corrosion products and to gain an understanding of the incorporation and release of fission and actinide products into these products. Methods for estimating the thermodynamic properties of numerous uranyl compounds were developed to enable more reliable predictions of product equilibria. Studies of the corrosion products of natural uraninites have focused on understanding how the secondary alteration products can incorporate and retard release of important radionuclides present in spent fuel.

In a related study, the Notre Dame/ANL/University of Missouri–Rolla project (59960) is also exploring the effects of products of $UO_2$ oxidation on release of radionuclides. Their work involves structural characterization by X-ray diffraction of the new phases that form as a result of reactions of spent nuclear fuel. Based on their studies of the crystal chemistry, this group has predicted that several of the alteration phases can incorporate selenium-79, but that technetium-99 will not be immobilized. They have also developed techniques for synthesis of uranyl phases, and several new compounds were characterized. In addition, they are studying the possibility of ion exchange of cesium and strontium into various uranyl phases as another mechanism to retard release of radioactive products.

### Project Teams

**Lead Principal Investigator (Award Number)**

- University of Michigan
  PI: Rodney C. Ewing (59849)
- University of Notre Dame
  PI: Peter C. Burns (59960)
  Argonne National Laboratory
  University of Missouri–Rolla
- Los Alamos National Laboratory
  PI: David D. Breshears (60015)
  Colorado State University
  New Mexico State University
- Pacific Northwest National Laboratory
  PI: John M. Zachara (60355)
  Savannah River Ecology Laboratory
- Sandia National Laboratory–Albuquerque
  PI: James L. Krumhansl (60403)
  Pacific Northwest National Laboratory
  University of Colorado

## Mobility of Actinides in Surface Soils

The goal of a LANL/Colorado State University/New Mexico State University project (60015) was to quantify the mobility of soil actinides from wind erosion, water erosion, and vertical migration. Wind erosion was quantified using spatially distributed aerosol measurements and correlated with meteorological and groundcover conditions. Water erosion was quantified using rainfall simulator experiments to measure vertical and horizontal changes in the tracer distribution. Vertical migration was studied using tracers in soil columns to quantify the effects of various biological and weathering processes. These studies have shown that the relative importance of the three transport mechanisms can differ by orders of magnitude at different DOE sites. The results can be used to prioritize efforts to improve risk assessments and remediation activities at sites that have actinide contamination in surface soils.

## Mobility of Radioactive Cesium in the Subsurface beneath High-Level Waste Tanks

Substantial amounts of aqueous solutions containing cesium-137 have leaked into the ground beneath storage tanks at Hanford. Thus, it is important to have reliable information to predict whether the subsurface constituents will bind the cesium for a sufficient time to prevent groundwater contamination. A PNNL/Savannah River Ecology Laboratory project (60355) has used a combination of microscopy, solution phase thermodynamic measurements, and chemical modeling to study the adsorption onto various materials that are present in the subsurface underneath the tanks. Work has included studies of the thermodynamics of cesium exchange, desorption and fixation of cesium, cesium distribution in Hanford micas, and identification of cesium-sequestering minerals in contaminated Hanford sediments. Their results indicate that a significant fraction of the sediment-bound cesium becomes rapidly fixed and is not available for further migration.

## Determination of Risks of Residual Sludges Left in Decommissioned Waste Tanks

The focus of a SNL/PNNL/University of Colorado project (60403) is to elucidate how the aging of sludge in a high-level waste tank impacts radionuclide mobility. The first step was to prepare simulated waste materials similar to those produced by the four different schemes used for plutonium separation. The solids and solutions were characterized using X-ray diffraction, atomic force microscopy, and optical spectroscopy for determinations of the concentrations of various metals in solutions. Experimental studies were then undertaken to quantify the uptake and release of heavy metals and radionuclide surrogates from the sludges. These studies were designed to simulate what could occur after groundwater gained access to a tank that had been decommissioned using a grout fill.

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# GEOPHYSICS AND HYDROGEOLOGY

## IMPROVED NONINVASIVE TECHNIQUES FOR SUBSURFACE CHARACTERIZATION ARE ESSENTIAL FOR COST-EFFECTIVE REMEDIATION

A National Research Council report, *Research Needs in Subsurface Science (March 2000)*, states that "currently available indirect measurement methods are inadequate for location of most types of contaminants in the subsurface, and direct methods such as drilling are both expensive and limited in effectiveness." Several EMSP geophysics projects described here involve attempts to improve indirect techniques for better characterization of the shallow subsurface.

Two such projects have been investigating advanced seismic methods. One has focused on analysis of existing high-resolution data acquired at an open pit copper mine, new data acquisition at an Air Force base known to have organic contaminants in a channel in a clay layer, and data processing algorithm development. The other project was designed to examine the complementary site-characterization capabilities of shallow seismic reflection techniques and ground penetrating radar methods.

A third geophysics study involved an investigation of a very-early-time electromagnetic imaging system for imaging of the subsurface in media where ground penetrating radar provides insufficient penetration depth and other electromagnetic systems have insufficient resolution. In another study, researchers are exploring a subsurface imaging technique using high-frequency electromagnetic impedance measurements for imaging the electrical conductivity and dielectric permittivity of the shallow subsurface. This study will evaluate where this technique might be useful as well as develop a better definition of where it cannot be used reliably.

An EMSP hydrogeology project involved development of computational methods for optimizing groundwater pump-and-treat remediation systems. The major goal of this work was to incorporate uncertainty in the hydraulic conductivity of the aquifer into the algorithms to enable optimal remediation designs for the common circumstance in which there are uncertainties in the parameters that determine the best design.

**Geophysical Techniques for Subsurface Imaging**
A U.S. Geological Survey project (60162) is enhancing a very-early-time electromagnetic (VETEM) system for imaging of the shallow subsurface. Above, the prototype VETEM system, towed by an all-terrain-vehicle, is shown operating on Pit 4 at the Radioactive Waste Management Complex at Idaho National Engineering and Environmental Laboratory.

### PROBLEMS/SOLUTIONS

- High-resolution subsurface maps are essential for characterizing the geometry of fluid pathways and are thus essential for remediation efforts. An EMSP project was designed to advance the ability of shallow seismic investigations to produce high fidelity structural and material maps of the subsurface.
- Needs for improved technologies for nonintrusive or minimally intrusive methods for identifying burial ground contents, and boundaries have been cited at all major DOE sites. An EMSP project was designed to enhance a very-early-time electromagnetic system for imaging the shallow subsurface in media where other techniques do not have either adequate penetration depth or resolution.
- Shallow, three-component seismology and ground penetrating radar have not been used together to examine the same volume of the shallow subsurface. An EMSP project is using both techniques to assess whether they can be used to determine preferential permeability paths in sufficient detail to allow quantitative hydrologic predictions.

### ANTICIPATED IMPACT

- A new numerical approach, called robust optimization, allows for determination of the lowest-possible cost for the design of pump-and-treat systems for the common case when there is uncertainty in the value of the hydraulic conductivity.
- Knowledge of the effects of site-specific physical and chemical properties on seismic attenuation can assist in determining if seismic methods are viable for characterizing sites with heterogeneous subsurface structures. A long-standing goal in subsurface science is to combine noninvasive measurement techniques with numerical models to produce reliable predictions of contaminant migration.
- High-frequency electromagnetic measurements are being developed for imaging the electrical conductivity and dielectric permittivity of the shallow subsurface. If successful, this technique could be used for environmental applications such as detecting buried waste and monitoring containment structures.

# Technical Summary and Progress

## Geophysical Techniques for Subsurface Imaging

The objective of a Rice University project (60115) is to develop advanced seismic methods to characterize the upper 30 meters of the subsurface. Their work has focused on analysis of existing high-resolution data acquired at an open pit copper mine, new data acquisition at an environmental remediation site, and data processing algorithm development. Work at the remediation site, Hill Air Force Base in Utah, has involved characterizing a DNAPL-containing channel in a clay layer. The location and depth of the channel estimated from the seismic data corresponded closely to the assumed location based on available well data.

The goal of a University of Kansas/State University of New York–Binghamton project (60199) was to examine the complementary site-characterization capabilities of shallow seismic reflection techniques and ground penetrating radar (GPR) methods. Shallow seismic reflection methods have usually been capable of imaging the subsurface at depths from 2 to 30 meters. This group was able to image the subsurface at depths of 0.6 to 2.1 meters by using a single 100-Hertz geophone group interval of 5 centimeters and a single shot from a .22-caliber rifle as the source. They were also able to image the water table at a depth of about 2 meters using GPR. Other work consisted of applying the combined seismic and GPR techniques to characterization of the cone of depression around active irrigation wells.

### Project Teams

**Lead Principal Investigator (Award Number)**

- University of Vermont
  PI: George F. Pinder (60069)
- Rice University
  PI: Alan R. Levander (60115)
- U.S. Geological Survey–Denver
  PI: David L. Wright (60162)
  University of Illinois
- University of Kansas
  PI: Don Steeples (60199)
  State University of New York–Binghamton
- Lawrence Berkeley National Laboratory
  PI: Ki Ha Lee (60328)
  University of California–Berkeley

The objective of a U. S. Geological Survey/University of Illinois project (60162) is to enhance a very-early-time electromagnetic (VETEM) system for imaging of the shallow subsurface in media where ground penetrating radar (GPR) provides insufficient penetration depth and time domain electromagnetic systems yield insufficient resolution. The system has been tested at the Cold Test Pit and at Pits 4, 9, and 10 at INEEL and also at Denver over the subsurface structures from a former foundry. They developed accurate and rapid methods for modeling their antennas over conductive earth, and they devised methods for calculating fields from buried conducting and dielectric objects. Two- and three-dimensional inverse methods were investigated, and a fast one-dimensional inversion algorithm was applied successfully to VETEM data from Pit 9 at INEEL and from the foundry site.

Another subsurface imaging technique is being explored by a LBNL/University of California–Berkeley project (60328). They are developing a noninvasive method for accurately imaging the electrical conductivity and dielectric permittivity of the shallow subsurface using high-frequency electromagnetic impedance measurements. Initial field measurements were done at a site that was relatively conductive, so the electric field measurements were difficult to make. High-frequency impedance data were also made at two sites with a more resistive environment. An overall evaluation of the feasibility of the high-frequency impedance methods was to be presented in the final report of the project.

## Optimization of Pump-and-Treat Systems

The development of computational methods for optimization of groundwater pump-and-treat remediation systems is the objective of a University of Vermont project (60069). The proposed methodology will use a groundwater flow and transport model to determine the optimal locations and pumping rates for groundwater wells. The solution of the model is dependent on the assumed hydraulic conductivity of the aquifer, and the work of this project incorporates uncertainty in the conductivity in the optimization problem. Goals of this research are to find optimal designs for a system designed to contain a plume of contaminated groundwater as well as for a system designed to manage risk by decreasing the concentration of contaminants at specific locations.

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# BIOLOGICAL SCIENCES

## EMSP PROJECTS RELATE TO HEALTH SCIENCE, MICROBIAL SCIENCE, AND PLANT SCIENCE

The central purpose for all Environmental Management activities is to avoid deleterious effects to the health of humans, wildlife, and plants as a result of exposure to wastes at DOE sites. The 1997 EMSP projects in health science all involve studies that may lead to more precise risk assessments. One project involves fundamental research on the bioavailability of solvents in soils in order to reduce uncertainties in risk assessments for this very common source of contamination. Another project has developed monitors for radon, thorium, and uranium so that more reliable carcinogenic risk assessments will be available for workers at Fernald and other similar sites. Another project is building a stronger scientific basis for assessing risks associated with inhaled alpha-emitting particles and is particularly applicable to management of plutonium-contaminated sites. In addition to risk assessments for humans, reliable methods to assess risks to wildlife populations are also essential, and this is the objective of another health sciences project.

There are two microbial science projects that involve a remarkable bacterium that can grow in the presence of radiation levels that would be fatal to most organisms, including humans. Most microorganisms that are useful for biodegradation of organic pollutants cannot survive high radiation fields or the presence of heavy metals, so the objective of these projects is to engineer the radiation-resistant organism so that it can be used for remediation of organic wastes in the presence of radionuclides and other heavy metals.

A plant science project involves fundamental studies related to the mechanism that certain plants use for metal ion uptake. The goals are to design plants that can readily take up heavy metals from contaminated soils and to assess how metals move through the food chain.

**Health Science and Risk Assessment**
A New York University project (59882) has focused on developing two types of monitors to measure worker exposure to certain radioisotopes during remediation activities: (1) personal radon-222 and radon-220 monitors and (2) miniature particle size samplers. The monitors allow measurement of environmental and worker exposures in a noninvasive way. The personal radon-222 and radon-220 monitor is shown above. At left, the particle size monitor is shown deployed in a weather housing sampling at Fernald.

### PROBLEMS/SOLUTIONS

- No personal monitors for the inhaled aerosol particle size distribution of any radioactive nuclide have been available for use during DOE remediation activities even though aerosol particle size is the major determinant of the radiation dose to the lung. An EMSP project has devised personal aerosol and radon monitors and is using them in an extensive test of personal exposures during remediation activities at Fernald.
- Phytoremediation and other passive remediation technologies were cited in STCG Need SR00-3026 as desirable for very large areas that have low levels of metal and radionuclide contaminated soils. An EMSP project is exploring the fundamental mechanisms by which plants transport heavy metals, and this work may lead to the development of an improved design of plants for heavy metal uptake.

### ANTICIPATED IMPACT

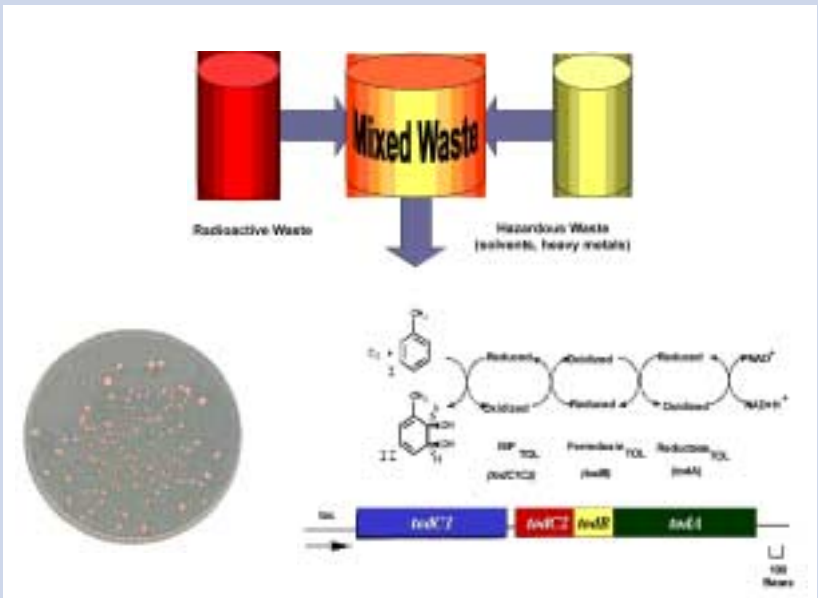
- An acute exposure to 500 to 1,000 rads is lethal to humans, but a bacterium that can grow continuously in the presence of chronic radiation at 6,000 rads per hour has been found. Two EMSP projects involve genetic engineering of this bacterium so that it can develop an ability to detoxify organic pollutants in the presence of radionuclides and heavy metals. Such microorganisms could address STCG Need AL-00-01-01-SC, for example, for treatment of soils contaminated with PCBs, radionuclides, metals, and other organic compounds.
- Remediation cleanup costs for contaminated soils depend markedly on the level to which the soils must be decontaminated. An EMSP project is conducting fundamental research on the risks associated with soils contaminated with organic solvents, and this work may lead to large savings by scientifically defining acceptable risk levels and thus avoiding unnecessary remediation efforts.
- The objective of another EMSP project is to help define the end points of remediation efforts so that remediation actions will be done to levels that prevent substantial damage to wildlife populations while avoiding wasteful actions that provide no measurable benefits.

## Health Science and Risk Assessment

Most organic contaminants within the DOE complex are in soil or water, so the University of California–San Francisco/ PNNL project (59828) was designed to investigate the uptake of some common organic pollutants when samples of contaminated soil or water were in contact with the skin of rats or humans. Real-time mass spectrometric breath analysis was used to quantitate chemicals in the exhaled breath stream. The exhaled breath data were evaluated using physiologically based pharmocokinetic models to estimate dermal permeability constants. These studies demonstrated that rat skin is about 40 times more permeable than human skin, that bioavailability is decreased when exposures are to contaminated soils rather than water, and that most of the test chemicals were lost to vaporization and not available for absorption if the soil or water samples were in contact with both skin and air.

A project at New York University (59882) has focused on the development of two types of monitors to measure worker exposure to certain radioisotopes during remediation activities. Personal radon-222 and radon-220 monitors have been designed, constructed, and placed in use at Fernald. This is the only such personal passive radon monitor in use at a DOE facility. Miniature particle size samplers have also been designed and constructed and placed into use at Fernald, and this device should have wide applicability at other DOE sites. This newly developed particle size monitor is the only one of its kind. The radon and particle size monitors provide the ability to measure environmental and worker exposures in a simple, noninvasive way. The sensitivities of the instruments are high enough to make measurements with normal background environments.

The main objective of a Lovelace Respiratory Research Institute project (59918) is to evaluate health risks due to inhalation exposure of the public to airborne dust that contains low amounts of plutonium dioxide ($PuO_2$). However, the project also provides research related to evaluating heath risks to workers who could have inhaled large amounts of plutonium and americium isotopes during accidents. A computer program to calculate the distribution of radioactivity intake via inhalation of $PuO_2$ by workers has been developed. A similar program has been developed for potential public or worker exposure by inhalation to $PuO_2$-contaminated, airborne dust. Results for worker exposure to large amounts of $PuO_2$ during accidents suggest that assessment of health risks to the workers related to radiation deterministic (nonstochastic) effects must consider that inhaled $PuO_2$ can lead to delayed health impairments without causing immediate harm. They have also computed intake distributions for $PuO_2$ inhaled in dust particles from Rocky Flats soils and suggested that respirable particles with diameters larger than 10 micrometers should not be excluded when establishing radionuclide soil action levels. Uncertainties in dose conversion factors along with other key uncertainties should be considered when developing soil remediation action levels. Finally, a possible large threshold for lung cancer induction was suggested as a result of examination of manuscripts and data related to workers at the Mayak plutonium production facility in Russia.




***Deinococcus radiodurans*:**
**Radiation resistant bacterium with added genes to detoxify hazardous organic component**

**Microbial Science and Genetic Engineering**

A University of Washington project (60150) is attempting to genetically engineer *D. radiodurans* to enable it to detoxify chlorinated organic compounds in mixed wastes. They have developed and tested tools for genetic manipulation of the bacterium to allow the construction and testing of optimized process strains for biotreatment of mixed wastes. Such strains should be amenable to above-ground treatment because they have high-level biodegradative capabilities with stable expression.

The objective of an ORNL project (60037) is to provide improved methods to assess risks from contaminants to wildlife populations. A database of avian and mammalian toxicity data has been assembled from literature sources. Next, an effort is underway to develop models to fit the literature-derived toxicity data for various species, and dose-response model development is being expanded to include a large number of chemicals of interest to DOE

sites. A related effort has been directed toward development of improved methods for extrapolating toxicity data from one species to another. The final task and a principal goal of the project is to relate toxic effects on individuals to population responses for the species. Simulations of population responses for 100 years were designed to evaluate potential differences in effects of contaminant exposure on bird species with different life-history strategies.

### Microbial Science and Genetic Engineering

Numerous microorganisms have been found to have the ability to degrade a variety of organic pollutants, but generally they are sensitive to radiation and do not function in wastes containing both organic materials and radionuclides or heavy metals. The bacterium *Deinococcus radiodurans* is the most radiation resistant organism known, but it does not detoxify organic pollutants. Two EMSP projects are attempting to introduce the genes from microorganisms that degrade organics into the radiation resistant organism. The researchers in the Uniformed Services University/University of Minnesota/PNNL project (59786) have constructed a recombinant *D. radiodurans* that expresses toluene dioxygenase, and this bacterium has the ability to oxidize toluene and several other compounds in a highly irradiating environment. They have also worked on constructing variants for the degradation of halogenated aromatic compounds and several other common pollutants. They also found that *D. radiodurans* requires certain amino acids for growth, but that this defect could be overcome by genetic engineering. In addition, they have developed a strain that can metabolize toluene or chlorobenzene while at the same time reducing toxic ionic mercury to elemental mercury. Researchers in a University of Washington project (60150) are also attempting to genetically engineer *D. radiodurans* to enable it to detoxify chlorinated organic compounds in mixed wastes. They have developed and tested tools for genetic manipulation of the bacterium to allow the construction and testing of optimized process strains for biotreatment of mixed wastes. Such strains should be amenable to above-ground treatment because they have high-level biodegradative capabilities with stable expression.

### Plant Science and Heavy Metal Remediation

Phytoremediation, the use of plants to remove toxic materials from soil and water, may prove to be a cost-effective solution for cleaning up metal-contaminated sites. Before plants can be optimized for metal remediation, detailed knowledge of how plants acquire metals is required. This is the objective of a Dartmouth College/University of Missouri–Columbia project (60271). Their work has concentrated on the genes for producing certain metal transporter proteins that play pivotal roles in metal ion transport in most species. The goals are to design plants that can readily take up metals from contaminated soils and to assess how metals move through the food chain.

### Project Teams

**Lead Principal Investigator (Award Number)**

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  University of Minnesota
  Pacific Northwest National Laboratory
- University of California–San Francisco
  PI: Ronald C. Wester (59828)
  Pacific Northwest National Laboratory
- New York University Medical School
  PI: Naomi H. Harley (59882)
- Lovelace Respiratory Research Institute
  PI: Bobby R. Scott (59918)
- Oak Ridge National Laboratory
  PI: Linda K. Mann (60037)
- University of Washington
  PI: Mary E. Lidstrom (60150)
- Dartmouth College
  PI: Mary Lou Guerinot (60271)
  University of Missouri–Columbia


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# INORGANIC AND ACTINIDE CHEMISTRY

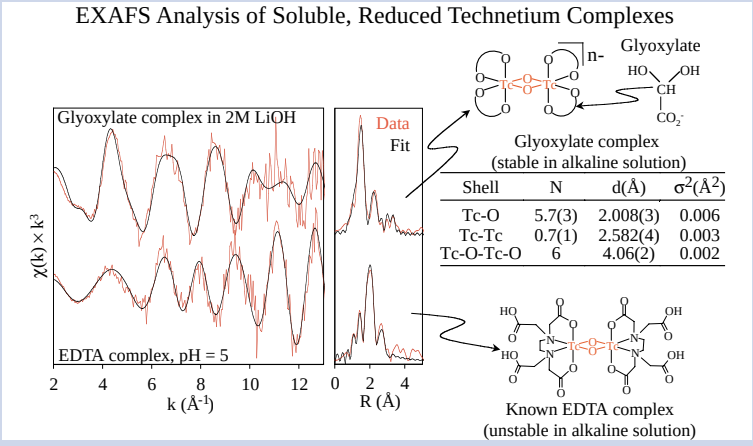
## ALMOST ALL RADIOISOTOPES IN DOE WASTES ARE INORGANIC MATERIALS, AND A THOROUGH UNDERSTANDING OF THE CHEMISTRY OF THESE MATERIALS IS ESSENTIAL FOR THE DESIGN OF REMEDIATION STRATEGIES

Two EMSP projects are studying issues related to the stabilization and volume reduction of nuclear materials processing residues. One project is exploring the electrochemical generation of highly reactive reagents that can react with substrate-bound actinide species or with the ion-exchange resins that contain some residual actinide contamination. Another project is studying the thermodynamics of the vaporization of actinide species in order to determine whether thermal processes to destroy organic materials pose a danger of producing fugitive actinide emissions.

There are two projects with a primary focus on subsurface contaminants. The chemical form of actual plutonium contamination in Rocky Flats soils was studied by a project that showed that it was present as a very stable oxide that had a low probability of being transported off site. Another project was designed to explore the use of a naturally occurring radium isotope as a tracer for locating organic liquids in the subsurface.

The design of more selective agents to bind specific metal ions has always been a major challenge for extraction and clean up of the products of the plutonium production process, and a leading research group in this area is exploring better methods for sequestering plutonium(IV) and related species. Another group was investigating the mechanisms of hydrogen gas production by radiolysis of mixed wastes.

Another EMSP project is investigating the chemistry of technetium in order to assist in developing better methods for separation, storage, and immobilization of this radioisotope. Another project related to high-level wastes was attempting to develop metal ion templated polymers for the selective binding of several actinide ions. A third high-level waste project was designed to explore the consequences of peroxynitrite formation in high-level waste tanks.




| Shell | N | d(Å) | $\sigma^2$(Å$^2$) |
|---|---|---|---|
| Tc-O | 5.7(3) | 2.008(3) | 0.006 |
| Tc-Tc | 0.7(1) | 2.582(4) | 0.003 |
| Tc-O-Tc-O | 6 | 4.06(2) | 0.002 |

**Fundamental Chemistry of Technetium**
A Lawrence Berkeley National Laboratory project (60296) is investigating the fundamental chemistry of technetium. Areas of research include Tc chemistry in lower oxidation states with various ligands under conditions similar to those in high-level waste tanks, and the effect of the intense radiation field on the chemistry of Tc in aqueous solutions.

### PROBLEMS/SOLUTIONS

- As pointed out in an STCG needs statement (AL-09-01-18-Tanks-S), more than half of the technetium in some Hanford tanks is not in the pertechnetate form and therefore cannot be separated from other materials in the tanks by current methods. An EMSP project is exploring the fundamental chemistry of technetium under tank conditions, and this work may lead to improved waste-treatment methods for technetium.
- High-temperature treatment to remove organic materials from wastes that contain actinides is a potentially useful way to reduce the volume of such wastes. But fugitive emissions of actinide species due to such processing must be avoided, so an EMSP project is designed to determine whether or not high-temperature destruction of organics might also cause the vaporization of some actinide species.
- The production of hydrogen gas is a principal safety concern for the storage and transport of species that emit alpha and beta particles in contact with organic materials. An EMSP project is designed to explore the fundamental mechanisms of hydrogen product by radiolysis of polymeric materials in order to make reliable risk assessments.

### ANTICIPATED IMPACT

- The urgency for remedial treatments for low levels of plutonium in soils is determined by whether the plutonium is mobile. An EMSP project has studied the speciation of plutonium in soils at Rocky Flats and found it to be in the form of highly stable and immobile oxides.
- Agents that bind specific metal ions have been used since the beginning of plutonium production. The rational design of such sequestering agents is being explored by one of the leading laboratories in this area. Their work may lead to greatly improved selectivity for such agents and could lead to more efficient techniques for removing highly radioactive species from the complex mixtures found in waste tanks and in other mixed wastes.

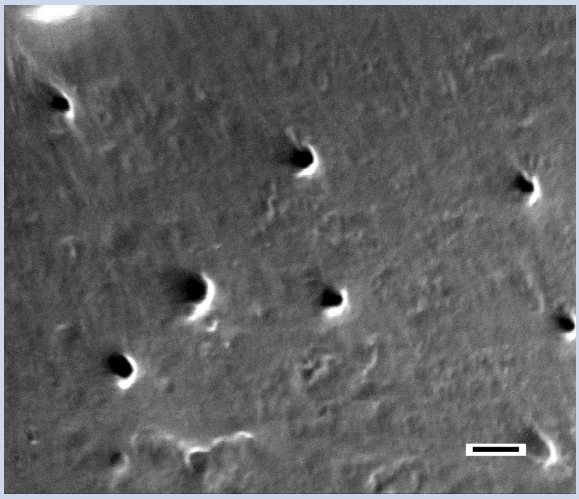
## Chemistry of Nuclear Material Wastes

*Stabilization of Nuclear Materials Processing Residues.* Mediated electrochemical redox reactions are being studied by a LANL/PNNL project (59967) to find improved methods for the stabilization and volume reduction of nuclear materials processing residues. The mediators employed for their studies have mostly been high oxidation states of cerium, silver, and cobalt that undergo redox reactions after having been formed electrochemically from stable starting materials. They have prepared samples containing actinides and actinide-surrogates on silica and titania substrates and have studied the electrochemistry of these substrate-bound samples. Both thermodynamic and kinetic parameters were measured in order to elucidate the influence of complexing ions on the redox properties of uranyl ions. Electrochemical techniques for destruction of widely used ion exchange resins have been developed. Studies of aluminum-containing substrates were also being done to study phases similar to those in the Hanford and Savannah River high-level waste tanks.

*Thermochemistry of the Volatilization of Actinides.* Organic compounds or resins that were used for chemical processing of actinides may be subjected to thermal treatment to volatilize the organic materials, leaving a greatly reduced volume of actinide-containing materials. The goal of an LLNL/UC–Berkeley project (60319) is to develop a basic thermochemical understanding of actinide volatilization behavior in such thermal treatment processes, i.e., can the treatment processes destroy the organics without producing fugitive emissions of actinide-containing species? A thermal transport furnace was used to study the volatilization of uranium dioxide in organic matrices subjected to gases containing argon, hydrogen, water vapor, carbon monoxide, and carbon dioxide. Some uranium transport was found to occur at temperatures as low as 600°C. Originally planned experimental work on the volatilization of transuranic actinides was refocused on the precipitation of Np(IV) oxide from Np(V) solutions as a function of temperature and pH. Though previously unknown as an aqueous precipitate, this phase formed at both 150 and 200°C, and solubility and kinetic data were obtained. The results suggest that for sufficiently long time scales (e.g., $10^2$-$10^5$ yr), Np(IV) oxide may be the long-term solubility-limiting phase for Np in groundwater systems, under both oxidizing and reducing conditions.

## Chemistry of Subsurface Contaminants

*Chemistry of Plutonium in Soils.* The goals of a LANL/ORNL project (59996) were to determine the chemical form and concentration of plutonium (Pu) in the environment at the Rocky Flats site, to study the chemistry of environmentally relevant Pu species and to model the environmental behavior of Pu. Based on isotopic ratio measurements, they determined that non-fallout Pu was localized directly east of the site and that there was no long-range contamination in other directions. The first definitive spectroscopic data on Pu in an environmental sample showed that Pu in the most concentrated samples was in the form of plutonium dioxide, a highly stable and immobile form. They have also compiled Pu thermodynamic data to obtain a database that is useful for modeling. One objective was to calculate the speciation of Pu(IV) under environmental conditions and to define conditions that may control the release of Pu from the dioxide.



**Templated Polymers for Selective Binding of Actinide Ions**
An Applied Physics Laboratory project (59977) is developing metal ion templated polymers for selective sensing and sequestering of uranyl and other actinide ions in aqueous solutions. The above photomicrograph shows a uranyl ion selective molecularly imprinted polymer membrane. The scale mark is one micron.

*Use of Radon as a Tracer for Organic Materials in the Subsurface.* Radon is produced by the decay of naturally occurring radium-226, and it occurs in groundwater as a dissolved gas. If the groundwater is in contact with an immiscible organic liquid, then the concentration of radon in the groundwater will be reduced because radon preferentially partitions into organic liquids. The Oregon State University project (60158) is investigating feasibility of using radon determinations from several groundwater sources in an area to locate organic liquids in the subsurface. Laboratory studies using a physical aquifer model suggested that the technique could detect the presence of an organic liquid. Field tests were conducted at a site in Oregon where perchloroethylene contamination was suspected, but the tests did not detect any organics. Initial studies of sites with known contamination gave ambiguous results, and work was continuing with those sites.

## Chemistry of Materials in Mixed Wastes

*Design of Metal Ion Sequestering Agents.* Complexing agents or ligands have been used for separating various metal ions since the beginning of plutonium production. Modern sequestering agents can have formation constants so large that effectively all of the metal ions in solution can be bound to ligand molecules. An LBNL group has been among the leaders in developing metal-ion-selective sequestering agents, and their project (60370) is entitled “Rational Design of Metal Ion Sequestering Agents.” The work includes synthesis of new ligands and characterization and

evaluation of these materials. They developed new synthetic routes to produce a variety of catechol-based ligands and studied their extractant properties for iron(III), cerium(IV), and thorium(IV). These ions have been used as plutonium(IV) surrogates, but studies with plutonium are a major objective of this work. Development of liquid-liquid extraction to remove metal ions from aqueous solutions is being pursued with modifications of these ligands.

*Safety Hazards Produced by Radiolysis of Organic Materials.* Production of hydrogen gas is a potential safety hazard for storage of mixed wastes containing organic materials in contact with transuranic isotopes that emit alpha particles. The objective of a Notre Dame project (59934) is to measure production of gases produced in the proton, helium ion, and carbon ion radiolysis of some organic polymers to obtain fundamental mechanistic information on decomposition of these materials. They have measured molecular hydrogen yields in the radiolysis of several polymers, including polyethylene. The production of hydrogen induced by alpha-particle radiolysis was much greater than for the same energy deposition using gamma rays, i.e., 40% greater in polyethylene and 450% greater in polystyrene. Since hydrogen may be formed inside thick polymer samples, diffusion of hydrogen to the surface is also being investigated to improve long-term projections of total gaseous hydrogen release.

## Chemistry of Species in High-Level Waste Tanks

*Templated Polymers for Selective Binding of Actinide Ions.* An Applied Physics Laboratory project (59977) is attempting to develop metal ion templated polymers for selective sensing and sequestering of uranyl and other actinide ions in aqueous solutions. The idea is to use ligands for the metal ion that have a polymerizable group, such as vinylbenzoic acid. A ligand-metal ion complex is formed, and the complexes are then used in the formation of polymers of various formulations. The premise is that when the metal ion is removed from the polymer, the cavity that remains will be ideally suited for selective binding of the ion. These procedures have been tested for sequestration of uranyl ions, for production of ion-selective electrodes, and for selectively permeable membranes. Other work involves use of luminescent uranyl compounds to construct optical sensors for uranyl ions.

*Reactivity of Peroxynitrite in High-Level Tanks*. A BNL/Washington State University project (59982) was designed to delineate the extent and nature of the radiation-induced chemical modifications of Hanford waste during storage as well as to explore potential applications of peroxynitrite in remediation processes. They found that radiation-induced generation of peroxynitrite ($ONOO^-$) is an efficient process in both solid nitrates and in concentrated nitrate solutions, and that it can contribute significantly to the chemistry of Hanford wastes. It was concluded that $ONOO^-$ can be an important source of oxygen within Hanford waste and may contribute to the generation of nitric and nitrous oxides emitted from the tanks. Radicals produced by $ONOO^-$ reactions can contribute to chemical modification of the waste during storage. They have also found that applications of $ONOO^-$ for destruction of waste organics and for the oxidative removal of chromium appear to be promising.

*Fundamental Chemistry of Technetium.* Technetium-99 ($^{99}Tc$) is one of the radionuclides of major concern for disposal of high-level tank wastes. The half-life of $^{99}Tc$ is greater than 200,000 years, and in aerobic environments, the most stable form of Tc is the pertechnetate ion, which is very soluble and highly mobile in the environment. The goal of an LBNL/LANL project (60296) is to characterize the fundamental chemistry of Tc. Research areas include Tc chemistry in lower oxidation states with various ligands under conditions similar to those in high-level waste tanks and the effect of the intense radiation field on the chemistry of Tc in aqueous solutions. Partial results include discovering that pertechnetate is rapidly reduced by radiolysis, even in the presence of a large excess of nitrate, due to reduction of $TcO_4^-$ by $NO_3^{2-}$, which is produced by the reaction of nitrate with hydrated electrons generated by radiolysis. Among the ligands investigated, soluble, reduced Tc species can be prepared in highly alkaline solution only when diols are present, which suggests that soluble, reduced Tc species in alkaline solution are Tc(IV) alkoxides. When cements containing blast furnace slag were exposed to the atmosphere, the initially reduced Tc species slowly oxidized to pertechnetate, although this oxidation proceeded at slightly different rates depending on the presence of nitrate and nitrite. When cements were isolated from the atmosphere, pertechnetate was steadily reduced to lower valent species, regardless of the presence of nitrate or nitrite.

### Project Teams

**Lead Principal Investigator (Award Number)**

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  PI: David E. Morris (59967)
  Pacific Northwest National Laboratory
- Johns Hopkins University
  Applied Physics Laboratory
  PI: George M. Murray (59977)
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- Oregon State University
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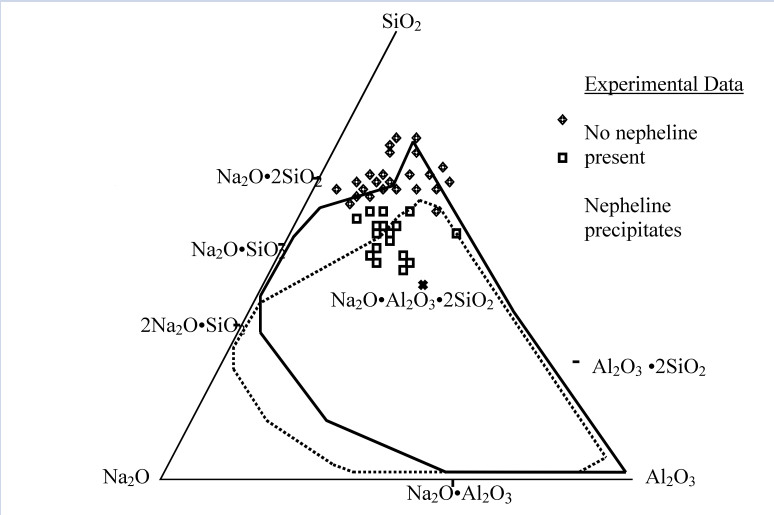
# MATERIALS SCIENCE

## IMPROVED MATERIALS AND PROCEDURES FOR LONG-TERM STORAGE OF RADIONUCLIDES ARE BEING DEVELOPED BY EMSP RESEARCH PROJECTS

Two EMSP materials science projects are directed toward the decontamination of metal surfaces. One project is attempting to compute diffusion constants of plutonium into steel so that the depth of penetration of plutonium into container surfaces can be predicted. The use of molten slags to remove radionuclide surface contaminants from stainless steel is being explored as a potential method to reclaim large amounts of stainless steel from DOE sites.

Most of the materials science projects involve development or characterization of materials for long-term storage of high-level wastes. One project has shown that crystalline silicotitanates can be loaded with cesium and then heat treated to form a stable medium for storage of cesium. These researchers also developed a new class of inorganic molecular sieves for strontium that are much more selective than previously available materials. The influence of irradiation on glass stability has been investigated by two projects and another has studied alkali ion exchange reactions in glasses exposed to water. Models of complex waste glass systems were developed by another research group to assist in the optimization of waste loading of glass. Electrochemical and spectroscopic techniques were being used by another group to explore the mechanisms of corrosion of the carbon steel tanks used for storage.

Two projects involved studies of materials for long-term storage of nuclear materials. One involved the first measurements of the thermodynamic properties of a number of potential waste form materials relevant to the storage of plutonium and other actinides, and another project explored the solubility limits of mixed actinide and neutron absorbers in a variety of ceramic and glass materials. Another program investigated radiolytic and thermal processes relevant to dry storage of spent nuclear fuels.




**Optimization of Waste Loading of Glass**
An Oak Ridge National Laboratory project (60020) is developing models of complex waste glass systems and spent fuel so that the composition, phase separation, and volatility of these systems can be predicted. Above: Ternary $Na_2O$-$Al_2O_3$-$SiO_2$ phase space (wt.%) showing the computed stability region for nepheline plus the glass phase at 800°C with no boria (¾) and 30 wt.% boria (¼). The comparison with experiment demonstrates that the model can predict important phenomena such as the precipitation of nepheline in glass.

### PROBLEMS/SOLUTIONS

- As described in STCG Need SR00-2032, the existing models for glass liquidus temperatures and glass durabilities have large uncertainties. Several EMSP projects were designed to explore these fundamental properties of waste-loaded glasses in order to optimize waste loadings.
- Cesium and strontium are responsible for a large fraction of the radioactivity of the materials in high-level waste tanks, and they must be separated and then stored in durable waste forms. A group of EMSP researchers has discovered that a simple heat treatment process of an inorganic ion exchange material can convert it to a waste form that is more durable than borosilicate glass for cesium retention, and they have also discovered a new class of inorganic ion exchange materials with better selectivity for strontium removal than any other material. Other applied research programs are already investigating uses for these results.

### ANTICIPATED IMPACT

- There are over a million tons of contaminated stainless steel and nickel within the DOE complex, and the D&D Focus Area has investigated several processes that could assist in the conversion of this large disposal liability into an asset worth an estimated $5 billion. An EMSP project is exploring some fundamental aspects of a melt decontamination process that could assist in the development of a practical recycling technology.
- According to a January 2000 DOE record of decision, at least 17 tons of surplus weapons plutonium will be converted to a mineral waste form and placed into a geological repository. Thermodynamics properties of actinide-bearing mineral waste forms must be known in order to predict the long-term stability of these materials, and an EMSP project was designed to provide the required thermodynamic data.

## Removal of Radionuclide Contamination from Metals

*Diffusion of Plutonium into Steel.* The goal of a West Virginia University/University of Connecticut project (59925) is to compute diffusion constants for plutonium into various steels or other metal alloys that may be used as a container for plutonium. The work involves electronic structure calculations to explore the stabilizing mechanism for face-centered-cubic plutonium, extraction of the information needed to perform dynamic simulations from electronic structure calculations, and use of this information to predict diffusion behavior. If the diffusion behavior can be predicted reliably, then the effects of temperature and time on the location of plutonium in steel or other structural materials can be anticipated prior to D&D work with materials that have been in contact with plutonium.

*Molten Slags for Decontamination of Metals.* The goal of a SNL/Boston University/Mining & Chemical Combine project (60363) was to investigate fundamental aspects of the use of molten slags to decontaminate radionuclide-contaminated stainless steel scrap metal. A typical slag is a mixture of calcium fluoride, calcium oxide, and aluminum oxide. One part of the work involved fundamental studies on electrochemical and thermochemical reactions among molten slags, metal, and surrogate contaminants. A surrogate of cerium oxide was found to be highly soluble in the molten slag, implying that similar radionuclide oxides would be removed from stainless steel surfaces. Experiments with nested pipe electrodes were used to determine the optimum furnace control strategy for decontamination of reactor coolant piping material, for example. Direct experiments to determine slag reactions with plutonium and uranium oxides were also performed and showed high refining coefficients for plutonium, uranium, and surrogate oxides. Also, practically no gaseous compounds of the elements contained in the metals were found as a by-product of the melting process. A molten slag-refining melting process is ready for demonstration.

## High-Level Wastes and Waste Tanks

*New Waste Forms for Long-Term Storage of Cesium and Strontium.* A new strategy for disposing of cesium-loaded crystalline silicotitanate (CST) ion exchangers was explored by several groups in a PNNL/SNL/UC–Davis project (60345). Standard ion exchange techniques were used to load cesium onto CST, and then heat treatment converted it to a waste form that was several orders of magnitude more durable than borosilicate glass for cesium retention. Detailed structural studies revealed the reasons for this stability. Heat treatment above 800°C also removed all molecular water, thereby eliminating the risk of radiolytic hydrogen production during storage. A class of new inorganic molecular sieves with extremely high selectivity for divalent metals was discovered, and these materials have orders of magnitude better selectivity for strontium ions under acid conditions than any other material. They are chemically and mechanically stable and can be thermally converted to refractory and unreactive ceramic materials.

**Molten Slags for Decontamination of Metal Surfaces**
A Sandia National Laboratory project (60363) researched fundamental aspects of the use of molten slags to decontaminate radionuclide-contaminated stainless steel scrap metal. This picture shows a decontaminated stainless steel ingot produced in an electroslag remelting furnace experiment at the Mining & Chemical Combine, Zheleznogorsk, Siberia, Russia. This experiment melted plutonium-contaminated scrap reactor coolant piping.

*Influence of Irradiation on the Stability of Glasses.* The suitability of glasses for nuclear waste disposal is dependent upon the ability of the glasses to resist phase separations or crystallizations that would result in the release of the immobilized materials. The major goal of a University of Arizona/PNNL project (59827) is to study the influence of irradiation and certain metal ions upon both the equilibrium and kinetic properties of glasses. They have investigated the influence of gamma radiation on phase transformation behavior, and they are comparing the growth behavior of irradiated glasses with non-irradiated samples. Other studies have involved the influence of iron oxides on the properties of the glass, and an unexpected result was that the ratio of iron(II) to iron(III) in the glasses had only a small effect on the measured properties.

*Radiation Effects in Silicate Glasses.* The objective of an ANL project (60313) is to understand the effect of ionizing radiation on the long-term stability of stored radioactive waste glass forms. The work has involved a

comprehensive electron paramagnetic resonance study of radiation-induced defects in several types of glasses. For example, it was shown that irradiation of alkali silicate glasses results in the formation of oxygen hole centers, silicon peroxy radicals, and silicon dangling bonds. However, their work implied that irradiation will not lead to mass migration of the modifier cations. The source of molecular oxygen bubble formation in the glass was identified, but the yield of oxygen is between $10^2$ and $10^4$ times less than previously estimated, so radiation-induced volatilization of the glass appears to be much less a problem than previously suggested. They have also studied the role of radiolytic hydrogen atoms in annealing the radiation damage in various glasses.

*Alkali Ion Exchange in Glasses.* The objective of a PNNL/LBNL project (60362) is to develop an understanding of the mechanisms that control alkali ion exchange in glasses when they are exposed to water and to correlate the rate of the ion-exchange reaction with glass structural properties. Glass-water reaction experiments indicated that the rate-limiting step in the ion-exchange reaction involves the transfer of a proton from the rupture of an O-H bond. Nuclear magnetic resonance and X-ray absorption techniques were used to explore structural changes due to changing glass formulations. A lower rate of sodium exchange is found as the amount of alumina in the glass is increased, and this was shown to be due to tighter bonding of sodium in the glass structure. The goal of these studies is to develop glasses that would be more resistant to the release of vitrified low-activity wastes.

*Optimization of Waste Loading of Glass.* The objective of an ORNL/Penn State University project (60020) is to develop models of complex waste glass systems and spent fuel so that the composition, phase separation, and volatility of these systems can be predicted. The impact of this work will be to assist in the optimization of waste loading of glass and to assess the durability of the waste forms. Volatility of various species during melter operations as well as corrosion of melter components can be predicted. A thermodynamic data-file has been developed for a number of multicomponent systems related to potential glass forms, and the range of compositions that can lead to formation of precipitates has been identified for certain glass formulations.

*Corrosion Mechanisms in Carbon Steel Tanks.* Many of the tanks used for storage of high-level wastes are made of carbon steel, and pitting of carbon steel can be induced by nitrate, sulfate, and chloride ions but inhibited by nitrite ions. The objective of a Savannah River/University of South Carolina project (60401) is to develop an understanding of the mechanism by which nitrite prevents corrosion so that more cost-effective corrosion prevention methods can be developed. Electrochemical techniques have been used to explore the effects of nitrate, chloride, and nitrite ions on the breakdown of the passive film on carbon steel. It was found that chloride-induced breakdown is mitigated by nitrite, which drives the breakdown potential higher. Although nitrate also induces pits in the passive oxide film on steel, the mechanism appears to be somewhat different from that of chloride. Spectroscopic studies were also being performed to explore the structural changes that occur in the passive layer due to pitting.

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- Pacific Northwest National Laboratory
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## Waste Forms for Actinides

*Thermodynamic Properties of Actinide-Bearing Minerals.* Knowledge of the thermodynamic properties (entropy, enthalpy and free energy of formation) of actinide-bearing mineral phases and potential decomposition phases is vital for fabrication of waste materials as well as for modeling the stability of the waste forms in a geological repository. A LANL/LLNL/UC–Davis project (60118) has been using a combination of calorimetric techniques to establish these properties for the potential waste form materials. Optimal experimental conditions were established using related, stable materials and this information was transferred to LANL where the actinide materials can be studied. Thermochemical properties of a large

number of materials have been determined and published, and future work may also include the determination of the energetics of mixing of the multicomponent solid solutions that have been proposed as the waste material for surplus weapons plutonium.

*Solubility of Actinides in Crystalline and Glass Matrices.* The goals of a PNNL/ANSTO/LBNL/University of Michigan project (60387) are to determine solubility limits of actinides and neutron absorbers in both crystalline and glass matrices and to determine the solution mechanisms for both types of systems. They have determined for the first time the solubility of plutonium and gadolinium oxides in an alkali boro-aluminosilicate glass under both reducing and oxidizing conditions, and the solution behavior of lanthanides in a variety of glasses has been studied because plutonium(III) and lanthanide(III) behavior is expected to be similar in these glasses. Solid solubility limits for uranium, plutonium, hafnium, and gadolinium have also been measured for a variety of potential ceramic host matrices. Based on their studies of plutonium, gadolinium, and hafnium behavior in both crystalline materials and glass melts, they have identified optimum formulations to incorporate the maximum amount of plutonium.

## Storage of Spent Nuclear Fuel

*Radiolysis of Water Adsorbed on Spent Fuel*. A PNNL/BNL/Rutgers University project (60392) involves basic research to assess potential hazards associated with long-term dry storage of spent nuclear fuel that is currently in storage in water across the DOE complex. Can chemically bound water that is still bound to the fuel after drying lead to long-term corrosion of the containers or fuel rods, generation of hydrogen and oxygen via radiolysis, or the formation of pyrophoric uranium hydrides? A detailed study of the interaction of water vapor with uranium dioxide at room temperatures indicated that adsorbed water is completely dissociated and that oxygen atoms are incorporated into the surface. Gamma radiation-induced degradation of water on a variety of oxide particle/water interfaces was studied. It was found that zirconia increases the hydrogen yield relative to pure gas-phase water, whereas other oxides had very little effect or even inhibited the formation of hydrogen. The breakdown of zirconia films under extreme radiation conditions was systematically studied to clarify the mechanism of oxygen removal from such surfaces.

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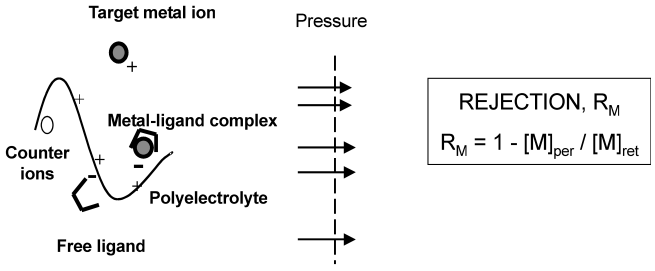
# SEPARATIONS CHEMISTRY

## CHEMICAL SEPARATIONS WERE ALWAYS AN IMPORTANT PART OF PLUTONIUM PRODUCTION TECHNOLOGIES AND ARE EQUALLY IMPORTANT FOR REMEDIATION

Even though the use of complexing agents for metal ions is a well-developed subject with a long history of applications at DOE sites, there continue to be new developments that may impact remediation activities. Many of the new techniques are applicable to separation needs in all the major areas of EM activities, so the classifications by focus area applications are not exclusive.

One of the recently developed separation techniques makes use of the formation of a colloidal particle composed of a positively charged colloid and a negatively charged ligand that binds a metal ion. The resulting microscopic particle can be separated from solution by ultrafiltration, which therefore removes the metal ion as well. Another new technique uses finely divided zero-valent metals on high surface area supports to reduce other metal ions as well as certain common organic pollutants. One EMSP research group has been working on the incorporation of metal-binding ligands into silica sol-gels. These "imprinted" sol-gels have high selectivity for strontium in the presence of calcium, for example, and may have other advantages over conventional organic ion-exchange resins. Another effort has been directed toward explorations of the use of coated electrodes as reversible ion-exchangers, particularly for use in dilute solutions.

The separation of technetium from other high-level wastes has been found to be more complicated than originally expected because the technetium in the tanks is not all in the form of the pertechnetate ion. One study described here has focused on the identification of the technetium species actually present in tank wastes in order to develop improved separation methods. Many tanks have organic complexants as well as inorganic materials, and another project has explored the importance of organic breakdown products on the separation of the various radionuclides in the wastes.




| Metal | $UO_2^{2+}$ | | $Th^{4+}$ | $Pb^{2+}$ | | $Cd^{2+}$ |
|---|---|---|---|---|---|---|
| Ligand | $CO_3^{2-}$ | DHBSA | DHBSA | DNTA | SNTA | $C_{11}HQ$ |
| $\%R_M$ | 99.9 | 99.9 | 99.9 | 99.8 | 99.7 | 99.6 |

**Ultrafiltration for Removal of Radionuclides**
A University of Oklahoma project (60041) involves use of ultrafiltration to remove radionuclide and other toxic metal ions from polluted water. Above: Diagram of ligand-modified polyelectrolyte-enhanced ultrafiltration process for removal of toxic metal ions from water. Separation efficiencies (rejection, $\%R_M$) are listed for metal ions and the ligands DHBSA (dihydroxybenzene disulphonic acid); DNTA (decyl-) and SNTA (sulfonato-nitrilotriacetic acid); and $C_{11}HQ$ (undecyl-8-hydroxyquinoline).

## PROBLEMS/SOLUTIONS

- Some methods proposed for the separation of technetium (Tc) from other high-level waste radionuclides assumed that all of the technetium would be present as the pertechnetate ion, but it is now known that much of the Tc in some tanks is in more reduced forms. An EMSP project is attempting to identify the chemical forms of Tc in the tanks so that more efficient separation procedures can be developed.
- A procedure for using tetraphenylborate (TPB) for removing cesium from high-level wastes was nearly ready for deployment when it was found that radiolysis to produce benzene presented unacceptable safety hazards. An EMSP project has explored a new procedure that minimizes the contact time between cesium and TPB so that the production of benzene is greatly reduced.
- Hydrothermal oxidations and a variety of vitrification techniques involve high-temperature processes that make spectroscopic investigations of the processes difficult. An EMSP project has made use of the Advanced Photon Source at Argonne Labs to make the first reported spectroscopic observations of aqueous redox chemistry in supercritical water.

## ANTICIPATED IMPACT

- As stated in D&D Work Package DD-02, there are currently 29 facilities at seven different DOE sites with more than 40 spent nuclear fuel storage pool facilities. Even though there have been numerous studies of basin cleanup technologies, an EMSP project involving the use of ultrafiltration for separation of soluble radionuclides may have advantages over previously developed methods.
- Iron filings have been widely used for reactive barriers to immobilize certain metal ions or to prevent chlorinated hydrocarbon migration. New reducing agents that contain zero-valent metals on high surface area supports are more reactive than iron filings and might be more efficient than previous techniques for a variety of separation and reactive barrier technologies.

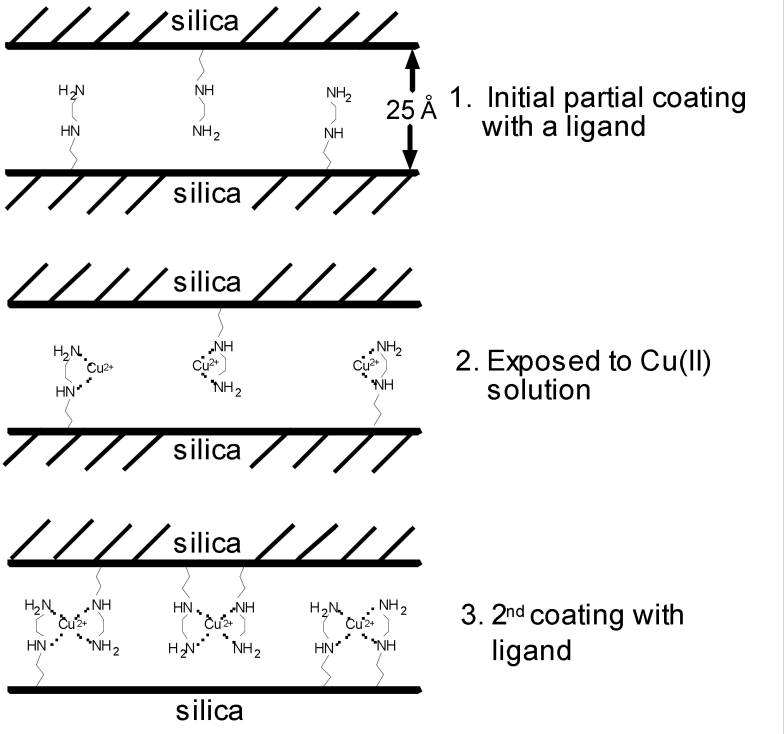
## Cleanup of Fuel Storage Pools

*Ultrafiltration for Removal of Radionuclides.* A University of Oklahoma/LLNL project (60041) involves the use of ultrafiltration to remove radionuclide and other toxic metal ions from polluted water. The procedure is to add a soluble cationic colloid along with an anionic ligand to the polluted waste water. If the ligand binds a target metal ion, then ultrafiltration of the colloid with its attached anionic ligand and metal ion removes the metal ion from solution. A system was demonstrated to remove 99.9% of uranyl from a neutral solution, a reduction of about a thousandfold in a single step. Other systems have shown similar results for removal of thorium, lead, cadmium, and mercuric ions, and methods for regeneration of the colloid and ligand were being investigated as well. These studies will also be used to guide similar work for removal of strontium and plutonium(IV) ions from solution.

## Separation of High-Level Waste or Mixed Waste Components

*Chemical Forms of Technetium in High-Level Tank Wastes.* The proposed method for separation of technetium (Tc) from Hanford tank wastes is based on Tc being present in the form of the pertechnetate ion ($TcO_4^-$). However, prior work with actual tank waste indicates that unidentified, reduced Tc species have been formed to a considerable extent and that these species are not easily converted to pertechnetate. A LANL/PNNL/Texas A&M project (59990) was designed to prepare and characterize a variety of Tc complexes that might be formed under tank conditions. A series of Tc(IV) complexes were prepared and found not to be stable under caustic conditions. Although the identity of the actual Tc species present in tank wastes had not yet been determined, a gluconate complex did have somewhat similar properties. They did find that 60% of the Tc in the AN-107 tank was not in the form of pertechnetate.

*Separations of High-Level Wastes that Contain Complexing Agents.* The overall objective of a LANL/New Mexico State University project (59993) is to provide a scientific basis for safely processing complexant-containing high-level tank wastes for disposal. Because studies with actual tank wastes are very difficult and expensive, they have emphasized methods for preparing realistic tank waste simulants that could be used to determine the importance of organic breakdown products on the partitioning of radionuclides. They have shown that the chemical environment of complexant-rich tank wastes is sufficient to cause reduction of pertechnetate, even in the absence of radiation. Isotopic tracer methods have been used to determine the mechanisms for degradation of various organic complexing agents. They have found, for example, that EDTA degradation can lead to hydrogen gas release or metal reduction.




**Stepwise imprint coating procedure led to enhanced target metal selectivity**

**Imprinted Sol-Gels for Binding Metal Ions**
A University of Tennessee project (60096) is preparing imprinted sol-gels containing specific metal-ion binding ligands. These hydrophilic oxide-base materials are expected to remove metal ions from water solutions faster than do organic ion-exchange resins.

*Ferragels for Separation and Removal of Contaminants.* Elemental iron filings have been widely used as a reducing agent for a variety of contaminants. The Penn State University/PNNL project (60017) has prepared a new class of reducing agents called Ferragels that consist of finely divided zero-valent metals on high surface area supports. They found with these reducing agents that Cr(VI), Pb(II), and Hg(II) were essentially quantitatively removed from dilute solutions of those metal ions. After 24-hour contact, 99% of pertechnetate was removed from a simulant solution at pH 13; the technetium was most likely reduced to Tc(IV). Ferragels along with small

amounts of nickel supported on carbon were about 15 times faster at removing trichloroethylene from solution than were iron filings, and the products appeared to be completely dechlorinated. Finally, an improved process for removing cesium from solutions using tetraphyenylborate (TPB) has been devised so that the radiolysis of TPB to form benzene does not occur to an appreciable extent.

*Reversible Ion-Exchange Electrode Coatings.* Traditional ion exchange methods for removing cesium from solution are effective, but chemical regeneration of the ion exchange bed can generate large volumes of secondary rinse and regeneration waste solutions. A University of Washington research program (60123) is exploring the use of nickel hexacyanoferrate coatings on electrodes as a new class of ion exchangers. The iron centers in the hexacyanoferrate can be switched between the ferrous and ferric states using an applied potential, and the material binds cesium in the ferrous state and releases it when converted to the ferric state. Thus, the material could potentially be used to remove cesium from a solution and release it into another without using any rinse or regeneration solutions. The research on this system has involved studies of the electrochemistry of the process as well as energy dispersive X-ray spectroscopy to interrogate the compositions of the thin films.

*Imprinted Sol-Gels for Binding Metal Ions.* The objective of a University of Tennessee/ORNL project (60096) is to prepare imprinted sol-gels containing specific metal-ion binding ligands. These hydrophilic oxide-base materials are expected to remove metal ions from water solutions faster than do organic ion-exchange resins. The group has investigated several different techniques for preparing the imprinted sol-gels, and has greatly improved the selectivity for binding certain metals. A crown ether with high affinity and selectivity for strontium has been encapsulated in sol-gels and could be recycled without loss of performance. Other ligands for binding cupric and mercuric ions also were effective and recyclable. Bimetallic titanium-silicon oxide systems have been prepared for the removal of cesium and uranyl ions from aqueous solutions.

*Spectroscopic Studies of High-Temperature Tank Wastes.* A 1996 EMSP project (54800) was awarded to a Pacific Northwest Consortium to develop a sector at the Advanced Photon Source (APS) at Argonne National Laboratory. A 1997 award (60050) to a University of Washington/PNNL group was made to utilize the high-intensity X-rays available at the APS to study chemical processes occurring during hydrothermal oxidations as well as the chemistry associated with tank waste vitrification. They studied the oxidation of chromium(III) to chromium(VI) at 400°C, and these were the first reported spectroscopic observations of aqueous redox chemistry in supercritical water. They have also shown that copper(II) has a strong tendency to oxidize other metals at high temperatures, and they studied high-temperature processes with tungstate and molybdate species. Both X-ray absorption and infrared absorption spectroscopies were used to explore the chemistry of chromate species at high temperatures.

## Project Teams

**Lead Principal Investigator (Award Number)**

- Los Alamos National Laboratory
  PI: Norman C. Schroeder (59990)
  Pacific Northwest National Laboratory
  Texas A&M University–Commerce
- Los Alamos National Laboratory
  PI: Rebecca Chamberlin (59993)
  New Mexico State University
- Pennsylvania State University
  PI: Thomas E. Mallouk (60017)
  Pacific Northwest National Laboratory
- University of Oklahoma
  PI: John F. Scamehorn (60041)
  Lawrence Livermore National Laboratory
- University of Washington
  PI: Edward A. Stern (60050)
  Pacific Northwest National Laboratory
- University of Tennessee–Knoxville
  PI: Ziling Benjamin Xue (60096)
  Oak Ridge National Laboratory
- University of Washington
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# DEACTIVATION AND DECOMMISSIONING

## THERE ARE STRONG SAFETY AND ECONOMIC INCENTIVES FOR INNOVATIVE DEACTIVATION AND DECOMMISSIONING TECHNOLOGIES THAT MAY BE ACHIEVED THROUGH SCIENTIFIC RESEARCH

The statement above is a quote from the National Research Council's *Interim Report for the Committee on Long-Term Research Needs for D&D at DOE Sites (2000)*, where it is also noted that "the safety incentive is immediate for workers conducting D&D operations, and it will grow as DOE takes on the more challenging D&D tasks." Even though the Committee's recommendations were for new research efforts in some topics not covered by the existing EMSP projects, the 1997 awards discussed here are in the categories of characterization, decontamination, and robotic systems that were of primary interest to the Committee.

The objective of one project was to use electronic structure calculations to enable predictions of the diffusion of plutonium into other metals as a function of temperature. If known, these constants would provide guidance for decontamination as well as for the appropriate conditions for storage of plutonium in metal containers.

Two projects have their primary focus on research related to contaminated material recycle and disposition. One effort is directed toward studies of an electroslag remelting process for decontamination of stainless steel so that it can be reused for DOE storage needs or even for free release. Another research effort has explored fundamental aspects of laser ablation for cleaning concrete surfaces, and this work may also lead to improved methods for characterization of contaminants in concrete.

An EMSP project to develop an ultrafiltration method for removal of hazardous metal ions from water may contribute toward improved technologies in this well-studied area. Finally, robots will be widely used for remote-handled waste, so the detection of impending robot failure is important for efficient D&D operations, and this is the subject of one EMSP project.

**Laser Ablation**
A project at Argonne National Laboratory (60283) has explored use of laser ablation for cleaning concrete surfaces. In this photo, the beam from the laser, which is 10 feet away, is being sent through a fiber-optic cable to a focusing head (the black cylinder at the top) containing lenses that focus the beam on the concrete. The bright light is an "ablation plume" of hot gases coming off the concrete (the laser beam is invisible). The impactor (the bronze cylinder on the left with its snout in the plume) collects and analyzes aerosol particles.

### PROBLEMS/SOLUTIONS

- As stated in a D&D work package (DD-12), weapons fabrication and assembly facilities contain large amounts of piping, ducts, tanks, and glove boxes contaminated with fissile materials. Therefore, an EMSP project has attempted to develop methods to predict the extent of the diffusion of plutonium into other metals so that guidelines for handling the contaminated materials could be made more reliable.
- Dismantlement of highly contaminated facilities will require extensive use of robots. One EMSP project has attempted to develop methods to provide early detection of impending failure in robots to avoid damage by a malfunctioning robot or expenses due to delays in cleanup activities.
- Removal of radionuclides and other metals from water is important to D&D of fuel storage pools and to many other areas within the EM mission, so this problem has been extensively studied for many years. However, new methods could still be useful because it is such a widespread problem, and the ultrafiltration techniques being explored in an EMSP project may lead to practical applications.

### ANTICIPATED IMPACT

- Large amounts of stainless steel and other metals will be required for long-term storage of DOE wastes. There are currently huge inventories of surface-contaminated stainless steel and nickel in the DOE complex with a value of up to $5 billion. An EMSP project is exploring one method for decontamination of these metals so that they could be used for waste disposal.
- DOE has 2,700 buildings, mostly constructed of concrete, so methods for characterization of contaminants in concrete as well as improved methods for surface decontamination are of great importance to the D&D effort. An EMSP project has investigated fundamental aspects of laser ablation of concrete surfaces, and the results may have an impact both on decontamination and characterization D&D projects in the future.

# Technical Summary and Progress

## Characterization

*Depth of the Diffusion of Plutonium into Container Surfaces.* Prior to beginning D&D work with materials that have been in contact with plutonium, it would be very useful to anticipate how much diffusion of plutonium into the steel or other container material has occurred. This is the problem being addressed by a West Virginia University/University of Connecticut project (59925) that is focused on electronic structure calculations to enable the predictions of the relevant diffusion constants as a function of temperature. The first stage of the work was directed toward providing a fundamental understanding of the stabilization of face-centered-cubic phase of plutonium, and detailed calculations leading to the prediction of diffusion constants were being performed.

## Decontamination

*Reclamation of Stainless Steel and Nickel.* It is anticipated that several million tons of stainless steel will be required for use in containers for DOE wastes. Large savings would accrue if the current DOE inventory of radionuclide-contaminated stainless steel and nickel could be recycled for this use, and a process to assist in achieving this objective is the subject of an SNL/Boston University/Mining & Chemical Combine project (60363). The major focus is on optimizing the electroslag remelting process to produce high quality ingots directly suitable for forging, rolling, and parts fabrication. Experiments and modeling studies with molten slags to remove contaminants such as plutonium and uranium oxides have been promising. This study, together with previous investigations in the D&D Focus Area, could lead to a practical technology with the potential to recycle contaminated materials worth up to $5 billion.

*Cleaning Concrete Surfaces by Laser Ablation.* The DOE complex contains large amounts of radioactively contaminated concrete, with most of the contamination within a few millimeters of the surface. An ANL project (60283) has explored the use of laser ablation for cleaning concrete surfaces as an alternative to the mechanical methods that expose workers to hazardous conditions. Their study has shown that pulsed lasers can remove material from concrete surfaces to any desired depth, but that it is more efficient to make many shallow passes rather than one slow, deep one. To generate the most desirable waste form, they showed that the laser must heat the material rapidly while avoiding melting the surface, so pulsed lasers are better than continuous lasers for this purpose. Because of fiber optic beam delivery, the laser can be far removed from the surface, and the only moving part is the focusing head, which is inexpensive and can be moved easily with a robot arm.

*Removal of Radionuclides from Fuel Storage Pools.* A University of Oklahoma/LLNL project (60041) involves the use of ultrafiltration to remove radionuclide and other toxic metal ions from aqueous waste solutions produced during decontamination operations. The procedure is to add a soluble cationic colloid along with an anionic ligand to the polluted wastewater. If the ligand binds a target metal ion, then ultrafiltration of the colloid with its attached anionic ligand and metal ion removes the metal ion from solution. A system was demonstrated to remove 99.9% of uranyl from a neutral solution, a reduction of about a thousandfold in a single step. Other systems have shown similar results for removal of thorium, lead, cadmium, and mercuric ions, and similar studies are anticipated for removal of strontium and plutonium(IV) from solution.

## Robotic Systems

*Early Detection of Impending Robot Failure.* A number of robotic systems have been explored for potential application to D&D problems in the DOE complex. For example, a hydraulic robot system was developed to deploy ORNL's Dual Arm Work Module and to use a variety of tooling for dismantlement operations (pipe shears, impact wrenches, grippers, $CO_2$ blasters, laser ablation systems, etc.). This system is described at the TMS site (http://ost.em.doe.gov/tms/Home/Entry.asp), Tech ID #1799. The Foster-Miller Technologies/Rice University project (60040) focused on developing a method to provide early detection, isolation, and tracking of impending faults in this robot. The purpose is to avoid damage to waste facilities by a faulty robot or failures of the robot that would cause delays in cleanup activities.

### Project Teams

**Lead Principal Investigator (Award Number)**

- West Virginia University
  PI: Bernard R. Cooper (59925)
  University of Connecticut
- Foster Miller Technologies, Inc.
  PI: Michael Martin (60040)
  Rice University
- University of Oklahoma
  PI: John F. Scamehorn (60041)
  Lawrence Livermore National Laboratory
- Argonne National Laboratory
  PI: Michael J. Pellin (60283)
- Sandia National Laboratory–Albuquerque
  PI: James A. Van Den Avyle (60363)
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# HIGH-LEVEL WASTES – CHARACTERIZATION, TANK SAFETY, AND INTERIM STORAGE

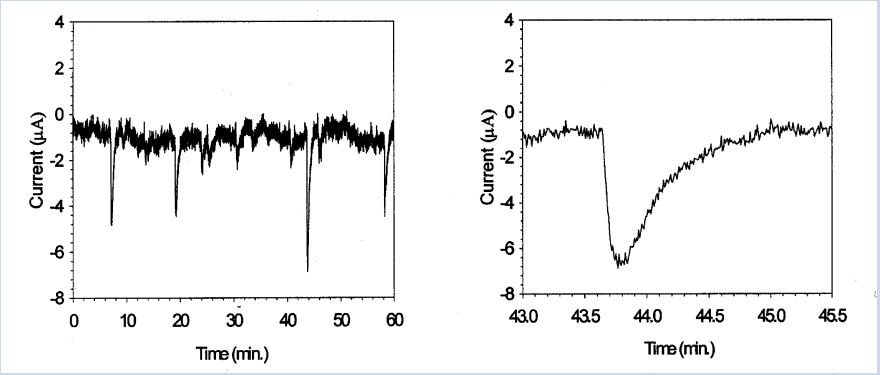
## CHARACTERIZATION OF HIGH-LEVEL WASTES REQUIRES THE MOST SOPHISTICATED TOOLS AVAILABLE TO MODERN ANALYTICAL SCIENCE

Descriptions of EMSP projects related to high-level wastes have been organized according to the key areas defined by the Tanks Focus Area (TFA), and EMSP projects most closely related to characterization, tank safety, and interim storage are discussed here. Projects that focus on retrieval, pretreatment, immobilization, and tank closure are discussed in a separate fact sheet. Of course, some basic research programs have relevance to several of these areas, and the division according to the TFA key areas is somewhat arbitrary.

Research programs in analytical techniques include applications of advanced chromatographic methods, thermospray mass spectrometry, laser ablation sampling for mass spectrometry, arrays of fluorescence sensors for direct sensing of metal ions in tank liquids, and templated polymers for selective metal-ion sensing. Another project is directed toward the characterization of chemical modifications to wastes that occur as a result of radiation-induced generation of peroxynitrite in the tanks.

A high priority in the TFA is for science and technology to improve tank integrity monitoring and corrosion prevention. One of the 1997 EMSP projects has used a variety of electrochemical techniques as well as "electrochemical noise" monitors to explore aspects of corrosion of iron and carbon steel in tanks. Another effort has been toward studies of corrosion prevention mechanisms with the goal of developing more cost-effective corrosion inhibitors. Another major tank safety issue is the buildup of flammable gases, and a diverse group of scientists has worked on improved methods for determining the amount of retained gas in the tanks.

The high-temperature behavior of INEEL's calcined waste must be understood prior to processing of those materials, and this is the subject of another EMSP project.




**Electrochemistry of Tank Corrosion**
A Pennsylvania State University project (60219) has explored fundamental aspects of passivity of iron as well as electrochemical emission spectroscopy as a means of monitoring corrosion in a tank environment. The graphs above show typical transient data. Left: Typical transients in the (electron) coupling current from 5 to 52 hours after load application for AISI 4340 steel in 6M NaOH at 70°C. The negative going transients are due to individual fracture events occurring at the crack tip. Right: Higher resolution view of a typical transient. The transient consists of a sudden increase in the coupling current followed by a slow relaxation. This type of transient is best explained by brittle fracture at the crack tip.

### PROBLEMS/SOLUTIONS

- From 1944 to 1989, plutonium was extracted at Hanford from 110,000 tons of uranium fuel at five different reprocessing facilities. Thus, the composition of the wastes in the 177 tanks at that site is quite variable and also not the same as in the major storage facilities at other sites. Therefore, complete characterization of the chemical and physical properties of this high-level waste requires the development of sophisticated new analytical techniques.
- As described in a TFA Science Need (AR-WT-11-01), the development of calibration standards, calibration procedures, and method validation for laser ablation methods for analysis of high-level waste is required. An EMSP project has studied fundamental mechanisms of the laser ablation process so that this need can be satisfied.

### ANTICIPATED IMPACT

- Characterization of a core sample of high-level tank waste can cost as much as a million dollars, and STCG Need RL-WT066 notes that a direct chemical analysis of constituents of tank waste could result in very large cost savings. An EMSP project is focused on the development of an ability to determine specific species directly inside a tank using a remote sensing device, and this would have both safety and cost benefits over existing techniques.
- The most serious accident with a high-level waste tank occurred in 1957 at Mayak, Russia as a result of an explosion of flammable gases formed in the tank. So knowledge of the amount of flammable gases retained in tank wastes is critical to safe management of tank ventilation, and three major laboratories have contributed to an EMSP experimental and modeling study of bubbles in sludges and slurries in the tanks.

# Technical Summary and Progress

## Characterization of High-Level Wastes

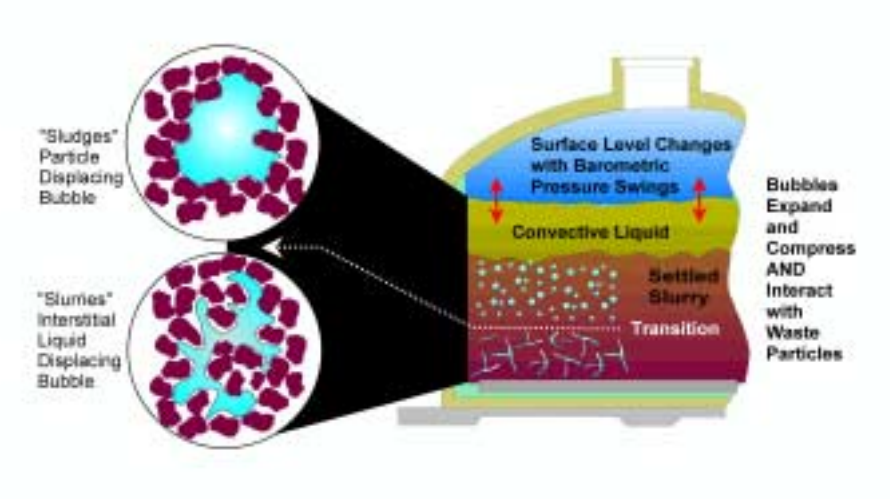
*Interactions between Metal Ions and Organic Complexing Agents.* The goal of an ORNL/University of Minnesota project (59978) is to improve characterization of the interactions between metal ions and organic complexing agents in tank wastes. The university group is working on chromatographic methods for separating the complexants, and the ORNL group is exploring the thermospray mass spectrometry of these species. The objective is to combine these efforts to improve characterization of the multicomponent mixtures that are present in most DOE wastes.

*Fundamental Mechanisms of Laser Ablation Processes.* A promising analytical method uses a laser pulse to introduce tiny particulates from the sample into a vapor stream that carries it into a plasma where it is vaporized and ionized for introduction into a mass spectrometer. Although this technique is particularly attractive for solid materials that are highly radioactive, laser ablation may not volatilize a sample and a calibration standard with the same efficiency, so the accuracy of the determination may be inadequate. A Washington State University/PNNL project (60075) has studied fundamental mechanisms of the laser ablation process in order to understand more clearly how to improve the quantitative accuracy of the technique for salt cake or vitrified waste forms.

*Determinations of Metal Ions in High-Level Tanks.* The determination of metal ions in high-level tanks with a sensor that could be inserted directly into a tank could offer both safety and cost advantages over the traditional core sampling methods. The objective of an ORNL/Tufts University project (60217) is to prepare a series of crown ethers that preferentially bind certain metal ions. Each of these would then be incorporated into a polymer matrix that is attached to the end of a fiber-optic cable, and a bundle of these fibers with different complexing agents would constitute the array sensor. Detection would be based on enhanced fluorescence that occurs when a metal ion is bound. The goal is to test an imaging fiber with an array of sensor sites selective for cesium, sodium, and potassium ions. If successful, the sensors would then need to be tested for stability under the high radiation levels found in the tanks.

*Templated Polymers for Selective Metal Ion Sensing.* Some DOE sites have been contaminated by a variety of water-soluble metal wastes, so methods for assessing the extent of contamination are needed along with remediation methods that do not increase the total volume of waste. An Applied Physics Laboratory project (59977) is attempting to develop metal ion templated polymers for selective sensing and sequestering of uranyl and other actinide ions in aqueous solutions. A ligand-metal ion complex is formed and then used in the formation of polymers of various formulations. The premise is that when the metal ion is removed from the polymer, the cavity that remains will be ideally suited for selective binding of the ion. These procedures have been tested for sequestration of uranyl ions, for the production of ion-selective electrodes, and for selectively permeable membranes. Other work involves the use of some luminescent uranyl compounds to construct optical sensors for uranyl ions.

*Radiation-Induced Chemistry of Peroxynitrite during Waste Storage*. A BNL/Washington State University project (59982) was designed to delineate the extent and nature of the radiation-induced chemical modifications of Hanford waste during storage as well as to explore potential applications of peroxynitrite in remediation processes. They found that radiation-induced generation of peroxynitrite ($ONOO^-$) is an efficient process in both solid nitrates and in concentrated nitrate solutions. It was concluded that $ONOO^-$ can be an important source of oxygen within Hanford waste and may contribute to the generation of nitric and nitrous oxides emitted from the tanks. Radicals produced by $ONOO^-$ reactions can contribute to the chemical modification of the waste during storage. They have also found that applications of $ONOO^-$ for destruction of waste organics and for the oxidative removal of chromium appear to be promising.




**Retention of Flammable Gases in Tanks**
A Pacific Northwest National Laboratory project (60451) involves both experimental and modeling studies of bubbles in sludges and slurries in order to develop improved methods for estimating the amount of retained gas in the tanks and to determine how barometric pressure fluctuations induce slow upward migration and release of gas bubbles.

## Tank Safety

*Electrochemistry of Tank Corrosion.* Work at a Pennsylvania State University project (60219) has focused on the electrochemical aspects of tank corrosion, including general corrosion and pitting corrosion. This work has examined the fundamental aspects of the passivity of iron as well as exploring electrochemical emission spectroscopy (EES), commonly known as "electrochemical noise monitoring," as a means of monitoring corrosion in a tank environment. Penn State researchers are exploring fundamental aspects of stress corrosion cracking in AISI 4340 steel (simulating a heat affected zone adjacent to a tank weld) in concentrated caustic environments. By measuring the coupling current that flows from a crack to the external surfaces, the PSU researchers have been able to detect and characterize for the first time *individual* fracture events occurring at the crack tip. The individual fracture events give rise to a sudden increase in the coupling current (in the negative direction) followed by a slow relaxation. Transients of this type are best explained by brittle fracture, most probably involving embrittlement of the matrix ahead of the crack tip by hydrogen. The dependence of the event frequency on potential, hardness, and hydrogen content should provide an unequivocal answer to the vexing question of whether fracture in this material is due to stress corrosion cracking or hydrogen embrittlement.

*Role of Nitrite in Prevention of Corrosion of Tanks.* Many of the tanks used for storage of high-level wastes are made of carbon steel, and pitting of carbon steel can be induced by nitrate, sulfate, and chloride ions but inhibited by nitrite ions. The objective of a Savannah River/ University of South Carolina project (60401) is to develop an understanding of the mechanism by which nitrite prevents corrosion. This could lead to the development of more cost-effective corrosion prevention methods that have less impact on the vitrification of tank wastes. Electrochemical studies have shown that chloride-induced breakdown is mitigated by nitrite because it increases the potential required for breakdown of the protective passive layer on steel. Although nitrate also induces pits in the passive oxide film on steel, the mechanism appears to be somewhat different from that of chloride. The competition of nitrite and iron oxidation can partially explain the role of nitrite in corrosion prevention.

*Retention of Flammable Gases in Tanks.* The flammable gases hydrogen, ammonia, and nitrous oxide are slowly formed in high-level waste tanks, and bubbles of these gases are retained in the sludges and slurries in the tanks. Knowledge of the amount of retained gas is particularly important for assessing the flammable gas safety hazards associated with both active and passive waste operations. Accurate estimates of retained gas based on measurements of the changes of tank volume with barometric pressure changes are highly desirable because direct measurements are very difficult and expensive. A PNNL/LBNL/University of Texas project (60451) involves both experimental and modeling studies of bubbles in sludges and slurries in order to develop improved methods for estimating the amount of retained gas in the tanks and to determine how barometric pressure fluctuations induce slow upward migration and release of gas bubbles.

## Interim Storage

*Characterization of Calcined High-Level Waste.* The high-temperature behavior of calcined high-level waste is poorly understood, so analytical techniques for characterizing these materials are needed to support process development activities. The INEEL project (60424) involves the design and construction of a sophisticated mass spectrometer that will enable identification of the species present on the surface and in the bulk as a function of time and temperature. The new instrument is designed to enable investigations of both neutrals and ions that are vaporized from the surface in order to understand the surface and bulk chemistry. High-level waste forms may be at elevated temperatures for long times, so these studies are particularly relevant for predictions of the long-term stability of various waste forms.

### Project Teams

**Lead Principal Investigator (Award Number)**

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  Applied Physics Laboratory
  PI: George M. Murray (59977)
- Oak Ridge National Laboratory
  PI: John E. Caton (59978)
  University of Minnesota
- Brookhaven National Laboratory
  PI: Sergei V. Lymar (59982)
  Washington State University
- Washington State University
  PI: J. Thomas Dickinson (60075)
  Pacific Northwest National Laboratory
- Oak Ridge National Laboratory
  PI: Gilbert M. Brown (60217)
  Tufts University
- Pennsylvania State University
  PI: Digby D. MacDonald (60219)
- Westinghouse Savannah River Company
  PI: Philip E. Zapp (60401)
  University of South Carolina
- Idaho National Engineering &
  Environmental Laboratory
  PI: James E. Delmore (60424)
- Pacific Northwest National Laboratory
  PI: Phillip A Gauglitz (60451)
  Lawrence Berkeley National Laboratory
  University of Texas–Austin


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# HIGH-LEVEL WASTES – RETRIEVAL, PRETREATMENT, IMMOBILIZATION, AND CLOSURE

## Several basic science studies of high-level wastes have already led to testing of new technologies at DOE sites

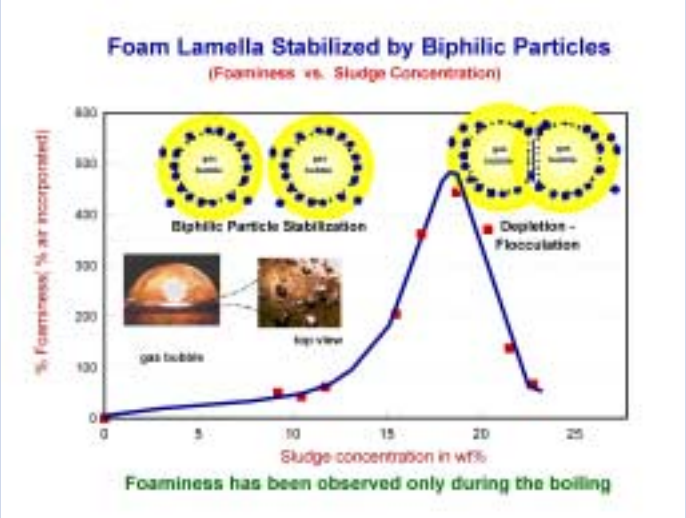
There were 22 EMSP projects awarded in 1997 that primarily addressed issues related to high-level wastes. Projects involving characterization of the wastes, tank safety issues, and interim storage are described in a separate fact sheet, and those that are most closely related to retrieval, pretreatment, and immobilization of high-level wastes as well as tank closure issues are discussed here.

The formation of foams is very detrimental to efficient processing of high-level wastes, and an EMSP project has focused on understanding the factors that cause foam formation. This work has led to an understanding of ways to develop better antifoam agents. Another group has worked to provide methods for safely processing tank wastes that contain organic complexing agents.

Two of the 1997 projects involve extensive studies of the chemical behavior of technetium in high-level wastes because it has more complex chemical behavior than many species in the tanks. Two other projects described here involve innovative methods for removal of a variety of metal ions from solution, and both may yield results of interest to subsurface contaminants and mixed wastes as well. Another study reported the first spectroscopic observations of redox chemistry in supercritical water and may lead to improved utilization of hydrothermal oxidations.

A multidisciplinary group from three laboratories has shown that a durable waste form can be made directly from an inorganic ion exchanger used to remove cesium aqueous solutions, and their basic work enabled them to discover new inorganic ion exchange systems with orders of magnitude better selectivity for strontium ions under acidic conditions. Four projects examined various aspects related to the long-term stability of glasses used for immobilization, and another focused on potential hazards due to groundwater access to tanks that have been closed and filled with grout.

**Formation of Foams during Waste Processing**
The objectives of an Illinois Institute of Technology project (60143) are to identify the factors that aggravate formation of foams and to identify ways to eliminate or minimize foaming. Based on the improved understanding of foam generation and stability, an improved antifoam agent was developed because commercial agents were ineffective.




### Problems/Solutions

- As stated in a Tanks Focus Area Science Need (S-WT-05-01), “technetium, one of the most problematic and long-lived contaminants of concern, presents retrieval, treatment, tank closure, and disposal problems, especially related to vadose zone and groundwater impacts.” Two EMSP projects were designed to study the chemistry of technetium under conditions similar to those in the tanks and to assist in developing better methods for separation of technetium from other tank wastes.
- Acceptance of vitrification for long-term storage is dependent upon knowledge of long-term waste glass performance, and another Science Need (S-WT-07-01) describes needs for studies of aqueous corrosion of glasses and corrosion in fractures and pores in glass. These are the subjects of several EMSP projects described here.

### Anticipated Impact

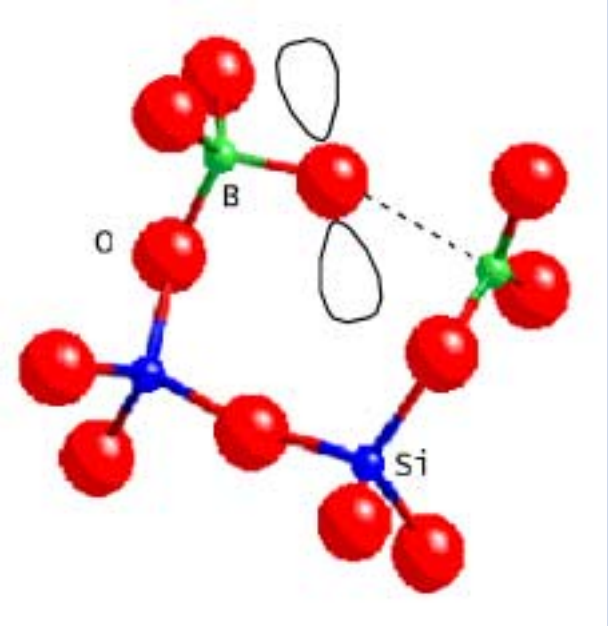
- An EMSP project demonstrated that a simple heat treatment of a crystalline silicotitanate ion exchanger can produce a highly durable waste form for retention of cesium, and the results of this work are already being evaluated as a method for cesium separation from tank waste at the Savannah River Site.
- The formation of foams can be a serious impediment to efficient processing of high-level wastes. A research effort focused on identifying the factors that promote the formation of foams has led to the development of an improved antifoam agent that is already being tested in a pilot plant at a DOE site.
- There are currently 282 tanks with about 90 million gallons of waste containing more than 700 million curies, and the life-cycle cost for remediation of these tanks is currently estimated to be $55 billion. So even modest improvements in cost-effective remediation technologies could result in substantial savings.

## Retrieval and Pretreatment of Tank Wastes

*Formation of Foams during Waste Processing.* The formation of foams can lead to slower production rates for high-level waste processes such as chemical processing, evaporation, and cesium decontamination. The objectives of an Illinois Institute of Technology project (60143) are to identify the factors that aggravate the formation of foams and to identify ways to eliminate or minimize foaming. They have found that the foaminess of sludge is due to the presence of colloidal particles and has a maximum as particle concentration is increased. For a given particle concentration, foaminess decays exponentially with an increase in particle size, and polydispersity in size leads to a reduction in foam formation. Based on the improved understanding of foam generation and stability, an improved antifoam agent was developed because commercial agents were ineffective. The new antifoam agent has been tested in both laboratory scale experiments and in a pilot plant at the Savannah River Site.

*Processing Complexant-Containing Tank Wastes.* The overall objective of a LANL/New Mexico State University project (59993) is to provide a scientific basis for safely processing complexant-containing high-level tank wastes for disposal. Because studies with actual tank wastes are very difficult and expensive, they have emphasized methods for preparing realistic tank waste simulants that could be used to determine the importance of organic breakdown products on the partitioning of radionuclides. They have shown that systems that contain pertechnetate along with some standard organic complexants and small amounts of the fission product metals ruthenium, rhodium, and palladium will result in almost quantitative reduction of pertechnetate to $TcO_2$, even in the absence of radiation. Isotopic tracer methods have also been used to determine the mechanisms for degradation of various organic complexing agents, and they have found, for example, that EDTA degradation can lead to hydrogen gas release or metal reduction.

*Fundamental Chemistry of Technetium.* Technetium-99 is one of the radionuclides of major concern for disposal of high-level tank wastes. The half-life of $^{99}Tc$ is over 200,000 years, and in aerobic environments the most stable chemical form is the pertechnetate ion, salts of which are highly soluble and highly mobile in the environment. The goal of an LBNL/LANL project (60296) is to characterize the fundamental chemistry of technetium. Partial results include discovering that pertechnetate is rapidly reduced by radiolysis, even in the presence of a large excess of nitrate. They have also found that soluble, reduced technetium species can be prepared in highly alkaline solution when diols are present, which suggests that soluble, reduced technetium species in alkaline solution are Tc(IV) alkoxides. In studies of cements containing blast furnace slag, the most important factor was found to be oxygen. When cements were exposed to the atmosphere, the initially reduced technetium species slowly oxidized to pertechnetate although this oxidation proceeded at slightly different rates depending upon the presence of nitrate and nitrite. When cements were isolated from the atmosphere, pertechnetate was steadily reduced to lower valent species, regardless of the presence of nitrate or nitrite.




**Effects of Radiation on Long-Term Stability of Glasses**
An Argonne National Laboratory project (60313) has involved a comprehensive electron paramagnetic resonance study of radiation-induced defects in several types of glasses. For example, it was shown that irradiation of alkali silicate glasses results in the formation of oxygen hole centers, silicon peroxy radicals, and silicon dangling bonds. This illustration shows the structure of an oxygen hole center in borosilicate solid.

*Separation of Technetium from High-Level Wastes.* A LANL/PNNL/Texas A&M project (59990) was designed to prepare and characterize a variety of technetium (Tc) complexes so that the chemistry of Tc in the Hanford tanks could be clarified. The ultimate goal is to determine the best procedures for separation of Tc from Hanford tank waste, because the current procedures are based on Tc being in the pertechnetate ($TcO_4^-$) form. Prior work with actual tank waste indicates that unidentified, reduced Tc species have been formed to a considerable extent and that these species are not easily converted to pertechnetate. During the course of this work, it was found that 60% of the Tc in a sample from the AN-107 tank was not in the form of pertechnetate. Several reduced Tc complexes have been prepared and characterized, but none of them appeared to be identical to actual Tc species present in tank wastes. A gluconate complex did have somewhat similar properties.

*Coated Electrodes for Ion Exchange.* A University of Washington research program (60123) is exploring the use of nickel hexacyanoferrate coatings on electrodes as a new class of ion exchangers. The iron centers in the

hexacyanoferrate can be switched between the ferrous and ferric states using an applied potential, and the material binds cesium in the ferrous state and releases it when converted to the ferric state. Thus, the material could potentially be used to remove cesium from a solution and release it into another without using any rinse or regeneration solutions. A major effort in the research has been to develop films with higher capacities for cesium uptake, and a tenfold improvement in capacity (to about 40 micrograms of cesium per square centimeter of electrode surface) has been achieved. The research on this system has involved studies of the electrochemistry of the process and also energy dispersive X-ray spectroscopy to interrogate the structures of the thin films.

*Ferragels for Removal of Metal Ions from Solution.* A Penn State University/PNNL project (60017) has explored applications of a new class of reducing agents, called Ferragels, that consist of finely divided zero-valent metals on high surface area supports. They found that Cr(VI), Pb(II), and Hg(II) were essentially quantitatively removed from dilute solutions of those metal ions. After contact for 24 hours, 99% of pertechnetate was removed from a simulant solution at pH 13, and the technetium was most likely reduced to Tc(IV). Ferragels along with small amounts of nickel supported on carbon were about 15 times faster at removing trichloroethylene from solution than were iron filings, and the products appeared to be completely dechlorinated. Finally, an improved process for removing cesium from solutions using tetraphyenylborate (TPB) has been devised so that the radiolysis of TPB to form benzene does not occur to an appreciable extent.

*Spectroscopic Observations in Supercritical Water.* There have been almost no direct spectroscopic observations of the species present in high-temperature reactions such as those in supercritical water oxidations or in the reactions associated with tank waste vitrification. A University of Washington/PNNL project (60050) was designed to utilize the high-intensity X-rays available at the Advanced Photon Source at Argonne to study chemical processes at the high temperatures and/or pressures associated with such processes. They studied the oxidation of chromium(III) to chromium(VI) at 400°C, and these were the first reported spectroscopic observations of aqueous redox chemistry in supercritical water. They have also shown that copper(II) has a strong tendency to oxidize other metals at high temperatures, and they studied reactions of some tungstate species as examples of an oligimerization process that occurs with a number of similar compounds. Both X-ray and infrared absorption spectroscopies were used to explore the chemistry of chromate and molybdate systems at high temperatures.

### Project Teams

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## Immobilization of Tank Wastes

*Crystalline Silicotitinate as a Durable Waste Form.* Several groups of researchers in a PNNL/SNL/UC–Davis project (60345) have shown that a very durable waste form can be achieved by a simple heat treatment of a cesium-loaded ion exchanger with no additives. The heat treatment of crystalline silicotitinate (CST) yielded a waste form that was several orders of magnitude more durable than borosilicate glass for cesium retention. Detailed structural studies revealed the reasons for this stability. Heat treatment above 800°C also removed all molecular water, thereby eliminating the risk of radiolytic hydrogen production during storage. A class of new inorganic molecular sieves for divalent metals was also discovered, and these materials have orders of magnitude better selectivity for strontium ions under acid conditions than any other material. They are chemically and mechanically stable and can be thermally converted to refractory and unreactive ceramic materials.

*Influence of Radiation and Metal Ions on Glass Properties.* Microscopic phase separation has been shown to be detrimental to the stability and durability of nuclear-waste glasses, so the ability of glasses to resist phase separations or crystallizations has been studied extensively in Tanks Focus Area projects. The major goal of a University of

Arizona/PNNL project (59827) is to study the influence of irradiation and certain metal ions upon both the equilibrium and kinetic properties of glasses. They have investigated the influence of gamma radiation on phase transformation behavior, and they are comparing the growth behavior of irradiated glasses with non-irradiated samples. Other studies have involved the influence of iron oxides on the properties of the glass, and an unexpected result was that the ratio of iron(II) to iron(III) in the glasses had only a small effect on the measured properties.

*Effects of Radiation on Long-Term Stability of Glasses.* The objective of an ANL project (60313) is to understand the effect of ionizing radiation on the long-term stability of stored radioactive waste glass forms. The work has involved a comprehensive electron paramagnetic resonance study of radiation-induced defects in several types of glasses. For example, it was shown that irradiation of alkali silicate glasses results in the formation of oxygen hole centers, silicon peroxy radicals, and silicon dangling bonds. However, their work implied that irradiation will not lead to mass migration of the modifier cations. In addition, the yield of molecular oxygen is between $10^2$ and $10^4$ times less than previously estimated, so radiation-induced volatilization of the glass appears to be much less a problem than previously suggested. They have also studied the role of radiolytic hydrogen atoms in annealing the radiation damage in various glasses.

*Models of Waste Glass Systems and Spent Fuel.* The objective of an ORNL/Penn State University project (60020) is to develop models of complex waste glass systems and spent fuel so that the composition, phase separation, and volatility of these systems can be predicted. The impact of this work may be to assist in the optimization of waste loading of glass and to assess the durability of the waste forms. Volatility of various species during melter operations as well as corrosion of melter components have also been considered. A thermodynamic data-file has been developed for a number of two- and four-component systems related to potential glass forms, and the range of compositions that can lead to formation of precipitates has been identified for certain glass formulations.

*Glass Corrosion Mechanisms.* Plans for immobilizing low-activity tank wastes involve vitrification followed by long-term storage, so it is important to understand the glass corrosion mechanisms that control the release of radionuclides that have been incorporated into the glass. The objective of a PNNL/LBNL project (60362) is to develop an understanding of the mechanisms that control alkali ion exchange in these glasses when they are exposed to water and to correlate the rate of the ion-exchange reaction with glass structural properties. Glass-water reaction experiments indicated that the rate-limiting step in the ion-exchange reaction involves the transfer of a proton from the rupture of an O-H bond. Nuclear magnetic resonance and X-ray absorption techniques were used to explore structural changes due to changing glass formulations. A lower rate of sodium exchange is found as the amount of alumina in the glass is increased, and this was shown to be due to tighter bonding of sodium in the glass structure.

## Tank Closure

*Release of Heavy Metals and Radionuclides from Closed Tanks.* Removing the small amounts of sludge that remain in a high-level waste tank after the bulk of the waste is retrieved is extremely costly, so it is anticipated that some of the sludge will be left in the tank when it is filled with grout for closure. The primary focus of a SNL/PNNL/University of Colorado project (60403) is to elucidate how the aging of sludge impacts radionuclide mobility. The first step was to prepare simulated waste materials similar to those produced by the four different schemes used for plutonium separation. Experimental studies were then undertaken to quantify the uptake and release of heavy metals and radionuclide surrogates. These studies were designed to simulate what could occur after groundwater gained access to a tank that had been decommissioned using a grout fill.

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# TRANSURANIC AND MIXED WASTE

## IMPROVEMENTS IN THIS AREA ARE BEING DEVELOPED

The Transuranic and Mixed Waste Focus Area (TMWFA) has the primary responsibility for developing new characterization and treatment methods for the 165,000 cubic meters of mixed low-level and transuranic waste. The EMSP projects most closely related to this area are summarized below.

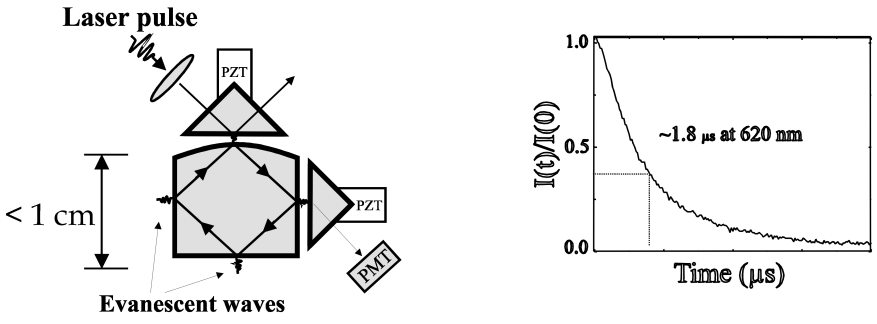
Several innovative analytical techniques are being developed for use in the characterization of mixed wastes. One project is exploring the use of membrane introduction mass spectrometry for detection of volatile and semivolatile organic compounds as well as organometallics. Another project provided the first quantitative evaluation of cavity ringdown spectroscopy for trace analysis, and detection limits were up to 300 times lower than with conventional atomic absorption methods. An innovative miniature spectrometer that can be placed at long distances from the light source and detector has been developed by another group, and they have been awarded several patents for this new technique.

The production of flammable gases is a potential safety hazard for the storage and transport of transuranic-containing mixed wastes, and another project has studied the production of gases as a result of radiolysis of organic polymers.

Studies related to nonthermal treatments of mixed wastes include one project that has developed innovative, new sequestering agents for selective removal of metal ions from solution and another project that has focused on the use of imprinted sol-gels for metal-ion removal. Another investigation has explored the use of a radiation-resistant bacterium to detoxify chlorinated organic compounds in the presence of radionuclides and other metals. Fundamental thermodynamic data for designing mixed waste separations are being determined in another project.

Thermal treatments of mixed wastes is sometimes very effective for destruction of organic compounds, and one EMSP project has concentrated on reactive capturing of volatile metals that may be produced by these processes.

**Evanescent Wave Cavity Ring-Down Spectroscopy**




**Miniature Spectrometer for Remote Chemical Detection**
A NIST project (60231) has involved a new type of attenuated total reflection spectroscopy similar to cavity ringdown spectroscopy (CRDS). Benefits of this technology include: (1) extremely high sensitivity, (2) both polarization states, (3) broadband, (4) wide T and P range, and (5) formation of a miniature, broadband, remote CRDS spectrometer.

## PROBLEMS/SOLUTIONS

- As described in STCG Need AL-09-01-19-MW-S, fundamental understanding is needed for the mechanisms that are responsible for gas generation in different types of packaged waste. This could lead to a reduction in cost, schedule, and regulatory compliance for shipment of transuranic-containing wastes to WIPP. One EMSP project was designed to study such a mechanism for radiolysis of a variety of polymers that are often used for packaging of wastes.
- "Basic instrumental…studies are needed to develop an on-line monitor that would sample directly in the offgas stream" of continuous emission monitors (STCG # ID-S.1.02). An EMSP project provided a quantitative evaluation of cavity ringdown spectroscopy for trace analysis and showed that the technique could be used to improve the detection limits of several classes of analytes.
- Another Mixed Waste science need (RL-MW027-S) stated that "analytical techniques for aqueous solutions and solid materials that can provide accurate results with 100 to 1,000 times less sample material than currently available technologies for the determination of organic constituents." Applications of a novel miniature spectrometer have been explored in one EMSP project, which has shown the ability to detect a small fraction of a monolayer of an absorbing material on one small crystal surface.

## ANTICIPATED IMPACT

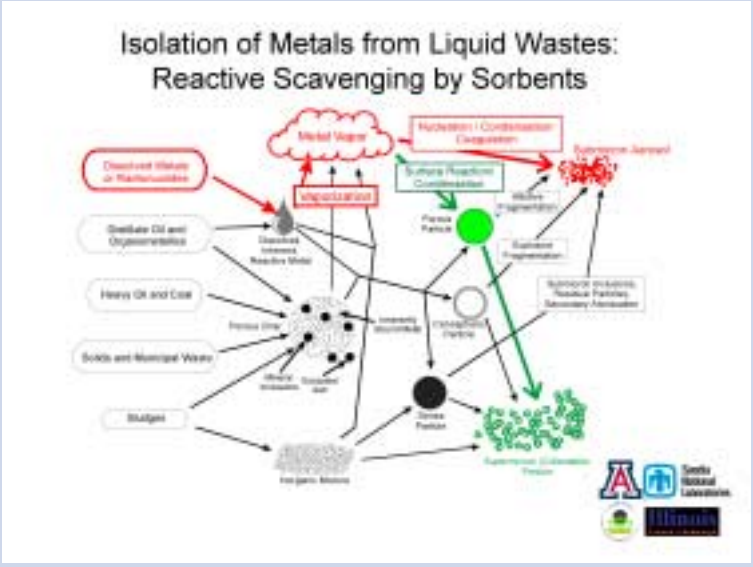
- Thirty-six DOE sites are currently storing about 165,000 cubic meters of mixed low-level and transuranic waste, and at least this much is expected to be generated by remediation activities over the next ten years. So basic scientific studies that lead to even small improvements in characterization or thermal and nonthermal treatment technologies can result in substantial cost savings.
- A high fraction of mixed waste contains chlorinated organics along with radionuclides. An EMSP research program is attempting to genetically engineer a radiation-resistant bacterium to enable it to detoxify chlorinated organics in mixed waste.

## TRU and Mixed Waste Characterization and Material Handling

*Membrane Introduction Mass Spectrometry.* A LANL project (59981) is exploring the use of membrane introduction mass spectrometry (MIMS) for the real-time characterization of organic and heavy metal contaminants in mixed wastes as well as potential applications of the technique for effluent monitoring of waste treatment operations. MIMS uses a polymer membrane as the interface between a liquid or gas and the vacuum in a mass spectrometer, and the technique has been widely used with volatile organic compounds. This research has found that chemical ionization of analytes using ions derived from oxygen or water is preferable to other ionization methods, and simultaneous detection of volatile, semivolatile, and organometallic compounds in air and water has been demonstrated with this technique. Several different types of membranes have been explored to enable more selective determinations of more polar and less volatile analytes.

*Cavity Ringdown Spectroscopy for Determination of Metals.* Cavity ringdown spectroscopy (CRDS) involves measuring the rate of decay of the light intensity in the cavity between two highly reflective mirrors as a function of the wavelength of the laser pulse. The goal of a Mississippi State University project (60070) was to provide the first quantitative evaluation of CRDS for trace analysis using inductively coupled plasma, graphite furnace, and cold vapor methods for introducing an absorbing analyte into the cavity. Early studies showed a detection limit for mercury of 20 parts per billion with an ICP method, as compared to a potential limit of 0.2 ppb. Detection limits for determinations of lead and mercury using graphite furnace atomization were found to be at least three times lower than those obtained by conventional atomic absorption methods, and a CRDS determination of mercury using a cold vapor method had a detection limit of 25 nanograms per cubic meter, which was over 300 times lower than that achieved with conventional atomic absorption methods. The technique could potentially be used to improve the detection limits of several methods for analysis of metals, including some radionuclides that are not easily detected by other methods.

*Miniature Spectrometer for Remote Chemical Detection.* Attenuated total reflection (ATR) has been widely used, particularly in infrared spectroscopy. A NIST project (60231) has involved a new type of ATR spectroscopy that is somewhat similar to the cavity ringdown spectroscopy described above. If a light pulse is introduced into a solid such that it is internally reflected at successive surfaces and thus travels in a ring, then the ATR phenomenon at one of the surfaces will result in a "ringdown" time that is shortened. Since the cavity uses only total internal reflection mirrors, a broad spectral bandwidth is accessible. As little as 0.006% of a monolayer of iodine on fused silica has been detected. An inexpensive diode laser source is being examined for construction of a cost-effective sensing system based on this concept. By locating the light source and detection system at distances up to a few kilometers through the use of fiber optics, this new technology could permit remote, high-sensitivity chemical sensing with a miniature spectrometer. Several patents have been awarded to this group for the development of this new technique for high sensitivity spectroscopy.




**High-Temperature Reactive Capture of Volatile Metals**
A potential technology for reducing the volume of mixed wastes is to use high-temperature reactive capture of volatile metals. A University of Arizona project (60326) is addressing several scientific issues relating to this technology. This illustration depicts variable pathways for a semivolatile radioactive metal. Red pathways are undesirable, and green pathways are environmentally benign. The project's work focuses on getting all the waste to follow the green pathway.

*Production of Gases by Radiolysis of Polymers.* The production of hydrogen gas is a potential safety hazard for storage of mixed wastes that contain organic materials in contact with transuranic isotopes that emit alpha particles. The objective of a Notre Dame project (59934) is to measure the production of gases produced in the proton, helium ion, and carbon ion radiolysis of some organic polymers in order to improve estimates of explosive or flammability hazards in the storage or transport of transuranic wastes. They have measured molecular hydrogen yields in the radiolysis of several polymers, including polyethylene. The production of hydrogen induced by alpha-particle radiolysis was much greater than for the same energy deposition using gamma rays, i.e., 40% greater in polyethylene and 450% greater in polystyrene. Since hydrogen may be formed inside thick polymer samples, the diffusion of hydrogen to the surface is also being investigated in order to improve long-term projections of total gaseous hydrogen release.

## Nonthermal Treatments of Mixed Waste

*New Sequestering Agents for Selective Removal of Metal Ions.* The separation of metal ions, particularly certain actinides, from organic compounds will be useful as a waste treatment technology if the extraction of the metal ions is quantitative into a small volume. A group at LBNL has been among the leaders in the development of metal-ion-selective sequestering agents, and their EMSP project (60370) is entitled "Rational Design of Metal Ion Sequestering Agents." Their work includes the synthesis of new ligands and the characterization and evaluation of these materials. They developed new synthetic routes to produce a variety of catechol-based ligands and studied their extractant properties for iron(III), cerium(IV), and thorium(IV). These ions have been used as plutonium(IV) surrogates, but studies with plutonium were planned and are a major objective of this work. The development of liquid-liquid extraction to remove metal ions from aqueous solutions is being pursued with modifications of these ligands.

*Imprinted Sol-Gels for Selective Removal of Metal Ions.* The objective of a University of Tennessee/ORNL project (60096) is to prepare imprinted sol-gels containing specific metal-ion binding ligands. These hydrophilic oxide-base materials are expected to remove metal ions from water solutions faster to organic polymers. The group has investigated several techniques for preparing the imprinted sol-gels, and has greatly improved the selectivity for binding certain metals. A crown ether with high affinity and selectivity for strontium has been encapsulated in sol-gels and could be recycled without loss of performance. Other ligands for binding cupric and mercuric ions also were effective and recyclable. Bimetallic titanium-silicon oxide systems have been prepared for the removal of cesium and uranyl ions from aqueous solutions.

### Project Teams

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- Lawrence Berkeley National Laboratory
  PI: Kenneth N. Raymond (60370)

*Microbial Treatment of Chlorinated Organic Compounds.* A University of Washington project (60150) is attempting to genetically engineer a radiation-resistant bacterium, *Deinococcus radiodurans*, to enable it to detoxify chlorinated organic compounds in mixed wastes. This bacterium has an unusually high ability to survive when exposed to high radiation levels, but the native organism does not convert chlorinated organic compounds to nontoxic species. The team has developed/tested tools for genetic manipulation of the bacterium to allow construction and testing of optimized process strains for biotreatment of mixed wastes. Such strains should be amenable to above-ground treatment.

*Thermodynamic Data for Design of Mixed Waste Separation Processes.* Some of the mixed waste inventory at DOE sites is aqueous waste, and knowledge of the basic thermophysical properties of these complex systems is needed to aid in designing treatment and disposal processes. One objective of the NIST/Michigan Tech University project (60155) was to develop and validate models that predict the phase equilibria and thermodynamic properties of hazardous aqueous systems. The models are intended for use in designing separation and treatment processes for mixed wastes, and they have been tested successfully with pure solvents, solvent mixtures, and mixtures that also contain salts. They are also conducting experimental measurements of thermophysical properties of a system that contains water, acetone, isopropyl alcohol, and sodium nitrate. Vapor-phase density and composition data for systems like this are almost nonexistent, and the new data will form the basis for designing mixed waste separation processes for which no design data have previously been available.

## Thermal Treatments of Mixed Waste

*High-Temperature Reactive Capture of Volatile Metals.* A potential technology for reducing the volume of mixed wastes is to use high-temperature reactive capture of volatile metals. This technology is potentially advantageous because organic compounds in waste are destroyed with high efficiency, the volume of metal-containing waste can be reduced considerably, and the process is applicable to a broad range of liquid wastes. The University of Arizona/ University of Illinois/EPA/SNL project (60326) is designed to address scientific issues relating to this technology. The experimental portion has shown how high temperatures can be used to capture reactively both cesium and strontium on substrates. A laser diagnostic system will enable in-situ measurements of solid, droplet, and vapor metal species. Modeling studies were underway to develop methods to predict both complete vaporization of all hazardous waste injected into a combustor and optimum placement of the injected sorbent to capture the metal vapor most effectively.


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# NUCLEAR MATERIALS

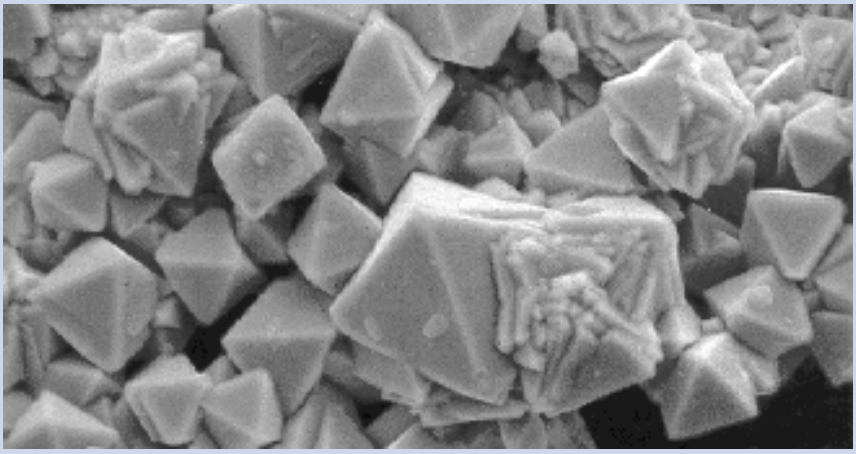
## THERE IS A LACK OF KNOWLEDGE AND EXPERIENCE IN DEALING WITH MANY ASPECTS OF NUCLEAR MATERIALS MANAGEMENT

The statement above was taken from the Nuclear Materials Focus Area (NMFA) Multi-Year Program Plan for FY00–FY04, which also notes that "the goal of the NMFA is to provide solutions that satisfy the technology needs for removing DOE's excess nuclear materials from EM sites. Materials management involves stabilization, safe packaging for storage and transportation, monitoring and surveillance activities and ultimate disposition." The materials of concern to the NMFA include transuranic isotopes, uranium, thorium, sealed sources, and all materials contained in the Defense Nuclear Facilities Safety Board recommendations 94-1 and 97-1.

One EMSP research program in this area has involved an extensive development of more reliable computational techniques for nuclear criticality safety analyses. The goals are not only to provide better safety evaluations but also to optimize operations related to the handling, storage, transportation, and disposal of fissile materials.

Fundamental thermodynamic properties of actinide waste forms have been studied by two projects. One has used calorimetric techniques to obtain the first measured values of thermodynamic properties for the materials related to the disposal of surplus plutonium, while another project has concentrated on measurements of solubility limits for plutonium and uranium along with neutron absorbers in both glass and ceramic matrices. The latter work has led to predictions for the formulations that could incorporate the maximum amount of plutonium.

Two projects have considered remediation processes that involve removing actinides from organic materials and might also have been discussed under the mixed waste category. One study explored possible volatilization of actinide species that might occur during thermal treatment of actinide-containing organic materials. Another project focused on improved methods for the stabilization of nuclear materials processing residues.



**Thermodynamics of Actinide Volatilization**
A Lawrence Livermore National Laboratory project (60319) involves experimental and thermodynamic modeling studies of actinide volatilization when mixed wastes are treated at high temperatures under reducing or oxidizing conditions. Above is a scanning electron microscopy picture of Np(IV) oxide crystals (octahedra) precipitated at aqueous solution of 200°C.

### PROBLEMS/SOLUTIONS

- Optimization of the loading of storage or transport canisters for nuclear materials requires nuclear criticality safety analyses for very complex geometries and mixtures of materials. A major EMSP research program has extended computational techniques to enable reliable safety analyses for a wide variety of materials and geometries.
- The fabrication of materials for storage of actinides requires knowledge of the thermodynamic properties of the materials. The first measured values of these properties for materials related to the disposal of surplus weapons plutonium were obtained in an EMSP research program.
- Ion exchange resins and other organic compounds that are contaminated with actinides may be subjected to high-temperature treatments to reduce the total volume of residues for long-term storage. One EMSP research effort was devoted to an exploration of potential safety hazards that might be associated with these procedures due to the vaporization of actinide-containing species.

### ANTICIPATED IMPACT

- A large amount of surplus weapons plutonium is to be converted to a mineral waste material and disposed of in a geological repository. Fundamental thermodynamic data for the waste materials is required both for optimizing the formulation of the waste materials and for modeling of the stability of these materials in the environment. An EMSP project has obtained the first experimental data for a large number of materials relevant to the storage of surplus plutonium.
- An EMSP research program has measured the solubility limits for plutonium oxides along with some neutron absorbers in both crystalline materials and glass melts. This data would be essential for the optimization of future programs to use these materials for long-term storage.

# Technical Summary and Progress

*Improved Nuclear Criticality Safety Analysis.* An ORNL project (60077) has worked on the development of more reliable computational techniques for nuclear criticality safety analyses. The goals are to provide basic knowledge that can lead to improved reliability of safety evaluations and to optimize operations related to the handling, storage, transportation, and disposal of fissile material. The new and improved computational capabilities enable the calculation of sensitivity coefficients of a system's neutron multiplication factor to perturbations in the cross section data using realistic 3-D models. The methodologies have be applied to systems with thermal, intermediate, and fast neutron spectra, mixed-oxide and uranium-fueled systems, and various geometrical configurations.

*Thermodynamics of Actinide Waste Forms.* Knowledge of the thermodynamic properties (entropy, enthalpy and free energy of formation) of actinide-bearing mineral phases and potential decomposition phases is vital for fabrication of waste materials as well as for modeling the stability of the waste forms in a geological repository. A LANL/LLNL/UC–Davis project (60118) has been using a combination of calorimetric techniques to obtain the first measured values of these properties for the materials related to the disposal of the surplus weapons plutonium. Thermochemical properties of a large number of materials have been determined and published, and future work may also include the determination of the energetics of mixing of the multicomponent solid solutions that have been proposed as the waste material for surplus weapons plutonium.

## Project Teams

**Lead Principal Investigator (Award Number)**

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  Pacific Northwest National Laboratory
- Oak Ridge National Laboratory
  PI: Cecil V. Parks (60077)
- Los Alamos National Laboratory
  PI: John Huang (60118)
  Lawrence Livermore National Laboratory
  University of California–Davis
- Lawrence Livermore National Laboratory
  PI: Tom Wolery (60319)
  University of California–Berkeley
- Pacific Northwest National Laboratory
  PI: Denis Strachan (60387)
  Australian Nuclear Science & Technology Organization
  Lawrence Berkeley National Laboratory
  University of Michigan

*Solubility Limits of Actinides in Crystalline and Glass Matrices.* The goals of a PNNL/ANSTO/LBNL/University of Michigan project (60387) are to determine solubility limits of plutonium (Pu) and uranium (U) as well as neutron absorbers such as gadolinium (Gd) and hafnium (Hf) in both crystalline and glass matrices and to determine the solution mechanisms for both types of systems. They have determined for the first time the solubility of plutonium and gadolinium oxides in an alkali boro-aluminosilicate glass under both reducing and oxidizing conditions, and the solution behavior of lanthanides in a variety of glasses has been studied because Pu(III) and lanthanide(III) behavior is expected to be similar in these glasses. Solid solubility limits for U, Pu, Hf, and Gd oxides have also been measured for a variety of potential ceramic host matrices. Based on their studies of plutonium, gadolinium, and hafnium behavior in both crystalline materials and glass melts, they have predicted optimum formulations to incorporate the maximum amount of plutonium.

*Thermodynamics of Actinide Volatilization.* Organic compounds or resins that were used for chemical processing of actinides may be subjected to thermal treatment to volatilize the organic materials, leaving a greatly reduced volume of actinide-containing materials. A LLNL/UC–Berkeley project (60319) involves a combination of experimental and thermodynamic modeling studies of actinide volatilization when mixed wastes are treated at high temperatures under reducing or oxidizing conditions. Experimental work on uranium dioxide in organic matrices has shown that some uranium transport can occur when gas mixtures of argon, hydrogen, water vapor, carbon monoxide, and carbon dioxide flow over the samples at temperatures as low as 600°C. In addition, the thermodynamic parameters for various uranium and plutonium vapor species were estimated. Originally planned experimental work on volatilization of transuranic actinides was refocused on precipitation of Np(IV) oxide from aqueous Np(V) solutions. Previously unknown as an aqueous precipitate, this phase was observed to form at both 150 and 200°C, and solubility and kinetic data were obtained. Np(IV) oxide may be the long-term solubility-limiting phase for Np in groundwater systems under oxidizing and reducing conditions.

*Stabilization of Nuclear Materials Processing Residues.* The goal of a LANL/PNNL project (59967) is to find improved methods for the stabilization and volume reduction of nuclear materials processing residues. They are exploring mediated electrochemical redox reactions for materials such as incinerator ash, combustibles, and other solid residues. To understand the influence of complexing anions on the redox properties of uranyl ions, both thermodynamic and kinetic parameters were measured. Electrochemical techniques for the destruction of widely used ion exchange resins have been developed. Studies of aluminum-containing substrates were also being done in order to study phases similar to those in the Hanford and Savannah River high-level waste tanks.

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# HEALTH / ECOLOGY / RISK

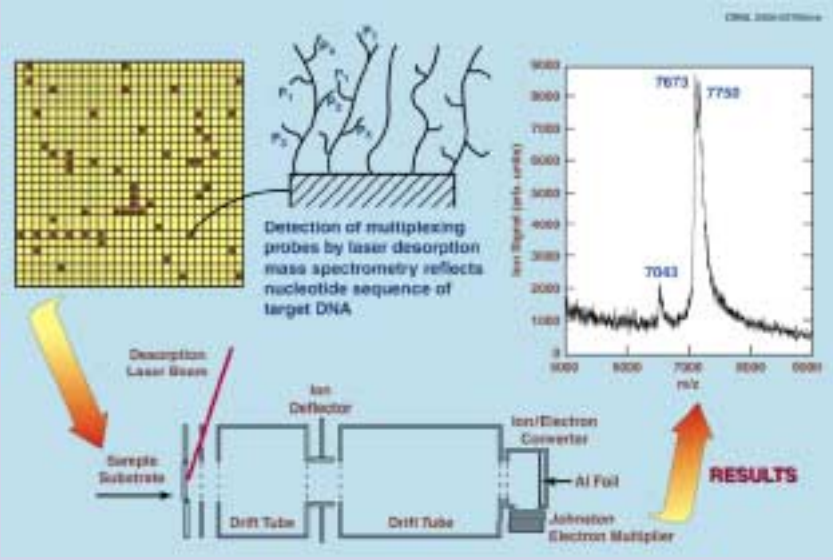
## THE GOAL OF ALL REMEDIATION ACTIVITIES IS TO PREVENT DELETERIOUS EFFECTS ON THE HEALTH OF ALL LIVING SPECIES IN THE ENVIRONMENT

It is almost always impossible to remove 100% of any contaminant from the environment, so the end point for remediation activities must be determined by a compromise between cost and risk, i.e., at what point will additional cleanup simply waste resources without significant reduction of risks?

Risks to health from alpha-particle-emitting species are mostly due to inhalation, but detection of these radioisotopes is also more difficult than for other radionuclides. One EMSP project investigated the effects of dust particle deposition on the performance of air monitors for alpha particles. Another explored better detectors for noble gas radionuclides that also improve discrimination between radon and other alpha emitters. A third project involved developing and testing of the only personal passive radon monitors in use at a DOE facility.

Hazards due to low levels of actinides in surface soils are a concern at several DOE sites, and two projects studied this issue. One concentrated on determinations of the mobility of actinides into surrounding areas, and the other worked on an evaluation of health risks due to inhalation exposure to dusts that contain low amounts of plutonium.

The relationship between exposure and health impact was the focus of two projects. One explored new mass spectrometric techniques for possible application to rapid screening for DNA mutation, and another project was designed to measure the uptake of some common organic pollutants when contaminated soils or water are in contact with the skin. The goal of another project was to assess risks from contaminants to entire populations of wildlife species.




**Rapid DNA Mutation Screening Using Mass Spectroscopy**
An Oak Ridge National Laboratory project (60218) used high throughput hybridization time-of-flight mass spectrometry to achieve multiplexing hybridization detection. The mass spectrum in the figure indicates three different probes with hybridization to the same template at a single site were detected. A genome-wide mutation survey can be pursued with this approach.

### PROBLEMS/SOLUTIONS

- A personal monitor for alpha contamination is required for a silo remediation project at Fernald, and STCG Need OH-F0002 says that use of such monitors would result in increased productivity and improved detection of contamination. An EMSP project produced a miniature passive alpha track detector for either personal or environmental distribution studies as well as an analyzer that measures air concentrations of alpha-emitting particulates and their size distribution. Both instruments have been deployed at Fernald.
- Public acceptance of DOE remediation efforts will require accurate risk assessments for residual contaminants at closed sites. The goal of one project is to improve capabilities for assessing health risks to the public associated with inhalation of aerosols that contain low levels of plutonium.
- Conventional techniques for introducing DNA molecules into mass spectrometers usually have poor resolution and are difficult to use for mutation analyses. An innovative new approach developed in an EMSP project has great potential for more convenient and reliable mutation analysis for environmental applications.

### ANTICIPATED IMPACT

- Clean up of soil actinides at DOE sites may cause ecological damage and waste billions of dollars if health risks are not decreased. An EMSP project is attempting to quantify the mobility of actinides in surface soil so that remediation activities can be targeted to areas where high risks can be demonstrated.
- A study of the permeability of human and rat skin to water and soils containing organic pollutants may lead to one or more orders of magnitude changes in acceptable risk levels at DOE sites, i.e., risk assessments can be based on more scientifically defensible models rather than more conservative estimates made on the basis of studies with pure compounds.

## Radionuclide Monitors

*Air Monitors for Detection of Alpha-Particles.* Continuous air monitors (CAMs) for detecting airborne plutonium and other radionuclides are frequently used in dusty environments, so it is particularly important to understand how the deposition of ambient dust particles on the CAM filters can interfere with the performance of the monitors. The New Mexico Tech/LANL study (60163) has been directed toward a careful evaluation of this issue, and they have found that when used only as an early warning detection device under high dust loading conditions, it may not be necessary to change the filters of CAMs as much as previously thought. They have also investigated self absorption in radioactive particles to help predict conditions under which degradation of alpha-particle spectral resolution may become important. They have developed a technique for generating convenient, short-lived radioactive aerosol particles for use in this or similar studies.

*Detectors for Radioisotopes of Noble Gases.* Radioisotopes of heavy noble gases (krypton, xenon, and radon) are produced by uranium, thorium, and transuranic wastes and by spent fuel. The primary objective of a Georgia Tech/ANL project (60474) is to develop better detectors for these isotopes with projected applications for long-term monitoring of wastes as well as alpha particle air monitors that discriminate between radon emissions and other alpha emitters. The first stage of the monitor will rely on a fluid transfer process in which heavy noble gases in the atmosphere are preferentially absorbed by certain organic fluids and subsequently degassed prior to detection. The team has found that sophisticated beta/gamma coincidence detection techniques result in higher sensitivity with lower background counts. A pulse processing system that allows dual-parameter pulse height analyses of coincidence events provides a superior ability to distinguish the different isotopes. The final result is intended to be fieldable systems consisting of a fluid transfer system and an optimized detection system. They have also found that by processing ambient air with a fluid transfer system, it may be possible to significantly reduce radon concentrations.

**Risks from Inhalation of Actinide-Containing Dusts** Corroded barrels have leaked plutonium (Pu)-contaminated oil onto the ground at Rocky Flats. A Lovelace Respiratory Research Institute project (59918) is contributing to improved characterization of health risks for DOE workers and the public from inhaled Pu.

*Personal Monitors for Alpha-Emitting Radionuclides.* Reliable personal monitors for exposure to alpha-particle emitting radionuclides have not been generally available for use by workers involved in DOE remediation activities. A project at New York University (59882) has focused on development of two types of monitors. Personal radon-222 and radon-220 monitors have been designed, constructed, and placed in use at Fernald. This is the only such personal passive radon monitor in use at a DOE facility. Miniature particle size samplers have also been designed and constructed, and this device should have applicability at a number of DOE sites. The radon and particle size monitors provide the ability to measure environmental and worker exposures in a simple, noninvasive way. The sensitivities of the instruments are high enough to make measurements with normal background environments, and extensive testing of the monitors is being done during remediation activities at Fernald. Additional work on these monitors is being pursued under a new project (74050).

## Risks from Actinides in Surface Soils

*Mobility of Actinides in Surface Soils.* The mobility of actinides in surface soils is a key concern for land-use planning at DOE sites, and plutonium mobility is a high visibility issue at Rocky Flats and Hanford. Over 500 DOE reports have included mention of actinide mobility, and a LANL/Colorado State University/New Mexico State University project (60015) was designed to assess plutonium mobility resulting from wind and water erosion and from vertical migration. They found that the relative importance of these transport mechanisms can vary by more than an order of magnitude across different sites. Disturbances that reduce ground cover can increase water and wind erosion by more than two orders of magnitude. They have also found that short-duration extremes in climatic and disturbance events may contribute the most to long-term risks. Improved risk assessments will require a better understanding and predictive capability for these low-frequency, high-impact events.

*Risks Due to Inhalation of Actinide-Containing Dusts.* The main objective of a Lovelace Respiratory Research Institute project (59918) is to evaluate health risks due to inhalation exposure to dusts that contain low amounts of plutonium dioxide, $PuO_2$. Some of their research also relates to worker exposure to large amounts of $PuO_2$ during accidents. Their computations suggest that inhalation intake of $PuO_2$ by Rocky Flats workers during accidents could vary by orders of magnitude, even for persons in the same room. These predictions are consistent with observations related to the recent accident at Los Alamos National Laboratory where workers inhaled $PuO_2$. The Lovelace results suggest that assessments of worker health risks due to inhaled plutonium must consider that inhaled $PuO_2$ can lead to delayed morbidity from non-cancer effects without causing immediate harm. Possible risks associated with long-term exposure after remediation and closure of a site such as Rocky Flats have also been examined. They have computed intake distributions for the public for $PuO_2$ inhaled in dust from Rocky Flats soils and suggested that respirable particles with diameters larger than 10 micrometers should not be excluded when establishing radionuclide soil action levels. Finally, they suggest that a possible large threshold for lung cancer induction should be considered when establishing radionuclide soil action levels. This could possibly help avoid wasting millions of dollars in unwarranted site cleanup operations.

### Project Teams

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- Los Alamos National Laboratory
  PI: David D. Breshears (60015)
  Colorado State University
  New Mexico State University
- Oak Ridge National Laboratory
  PI: Linda K. Mann (60037)
- New Mexico Institute of Mining & Technology
  PI: Stephen D. Schery (60163)
  Los Alamos National Laboratory
- Oak Ridge National Laboratory
  PI: Chung Hsuan Chen (60218)
- Georgia Institute of Technology
  PI: John D. Valentine (60474)
  Argonne National Laboratory

## Relationship between Exposure and Health Impact

*Rapid DNA Mutation Screening Using Mass Spectroscopy.* The goal of an ORNL project (60218) was to explore some innovative mass spectrometry techniques for possible application to rapid DNA mutation screening. This group developed an innovative approach to use laser-induced acoustic waves for DNA desorption, and they demonstrated that this technique has better mass resolution for both proteins and DNAs than does the conventional matrix-assisted laser desorption/ionization method. A better understanding of the relationship between exposure and health impact is an essential part of contaminant risk analysis, and a rapid screening technique would greatly improve the chances of finding the linkages between gene mutation and contaminants. They found, for example, high conservation between the p53 gene between humans and medaka fish, so measurements of mutation of fish due to contaminants can be used to assess the impact to humans by the same contaminants.

*Uptake of Organic Pollutants Resulting from Skin Contact.* Most organic contaminants within the DOE complex are in soil or water, so the University of California–San Francisco/PNNL project (59828) was designed to investigate the uptake of some common organic pollutants when samples of contaminated soil or water were in contact with the skin of rats or humans. Real-time mass spectrometric breath analysis was used to quantitate chemicals in the exhaled breath stream. These studies demonstrated that rat skin is about 40 times more permeable than human skin, that bioavailability is decreased when exposures are to contaminated soils rather than water, and that most of the test chemicals were lost to vaporization and not available for absorption if the soil or water samples were in contact with both skin and air. The objective of this work is to reduce uncertainties in exposure/dose models and to replace conservative default assumptions for risk assessments with more reliable information.

*Risks from Chemical Contaminants to Wildlife Populations.* The objective of an ORNL project (60037) is to provide improved methods to assess risks from chemical contaminants to wildlife populations. A database of avian and mammalian toxicity data has been assembled from literature sources, and models have been developed to fit the literature-derived toxicity data for various species. A related effort has been directed toward development of improved methods for extrapolating toxicity data from one species to another. A principal task of the project is to relate toxic effects on individuals to population responses for the species. Simulations of population responses for 100 years were designed to evaluate potential differences in effects of contaminant exposure on bird species with different life-history strategies. The objective of this work is to guide remediation activities to focus on remediation of contaminants with clearly defined risks to wildlife populations while avoiding unnecessary activities for cases in which the risks are low.


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# SPENT NUCLEAR FUEL

## EMSP RESEARCH PROGRAMS PROVIDE BASIC KNOWLEDGE REQUIRED FOR SAFELY MANAGING SPENT NUCLEAR FUEL

DOE-owned spent nuclear fuel includes fuels from Hanford and Savannah River reactors, naval nuclear propulsion fuel, research reactor fuel, and a small fraction of the commercial nuclear power reactor spent fuel. The National Spent Nuclear Fuel Program is planning to remove spent fuel from underwater storage and put it into temporary dry storage where it can be readied for transport when an underground repository is completed.

When the rods are removed from water and placed into dry storage, it is necessary to passivate them by a controlled exposure to air so that surface oxides can form. One of the projects described below was designed to develop flow visualization methods and reliable predictive techniques for the passivation treatment operations. The purpose of another project was to investigate water interactions with fuel rods and metal-oxide materials, to study the role of thermal processes and radiolysis in the generation of hydrogen and oxygen gases, and to examine the role of radiation-assisted corrosion during fuel rod storage.

Another group developed high-resolution, position-sensitive, gamma-ray detectors for direct imaging of spent fuels and fissile materials. Their system not only possesses imaging capabilities but also high-resolution gamma spectroscopy for rapid isotope identification.

Two projects investigated issues related to safe long-term storage of fuels in a repository. One study investigated potential corrosion products from long-term storage of uranium oxides under oxidizing conditions. A related study by another research group explored mechanisms for the release of radionuclides from stored fuel in order to improve estimates of the release of radioactive species over time.

**Passivation of Spent Fuel Elements**
A University of Idaho project (60144) has developed an experimental apparatus to simulate reactive flow patterns and has shown that reactions may decrease the likelihood that all corroded areas will be properly treated. At right: A mixture of hexanoic acid and mineral oil flows over an aluminum plate embedded with metallic sodium. The hexanoic acid and metallic sodium react to create hydrogen bubbles. Dye is injected upstream of the flow, and this photo illustrates the complex fluid interaction of buoyant bubbles and fluid moving horizontally.

### Problems/Solutions

- Reliable data concerning the release of radioactive species from spent fuel stored in a repository are essential for the design and licensing of the repository. Two EMSP projects are exploring the chemistry of uranium dioxide in spent fuel under repository conditions. Their work related to the mobility of radioactive fission products and transuranic elements in spent fuel may also be useful in the design of engineered barriers for the repository.
- The highest priority STCG Need related to spent fuels involves studies of chemical passivation of spent fuel elements after transfer from wet to dry storage (AL-09-01-21-SNF-S). An EMSP project involved three laboratories in an experimental and computational research effort to study the details of passivation treatment operations.

### Anticipated Impact

- Rapid characterization of spent fuel elements is required for nuclear materials accountability and for determinations of suitability for temporary or long-term storage. An EMSP research program has developed a system that not only possesses imaging capabilities but also has high-resolution gamma spectroscopy for isotope identification.
- Thousands of tons of spent nuclear fuel are in water storage across the DOE complex. When this material is removed and placed into dry storage, chemically bound water could lead to the generation of dangerous hydrogen gas or pyrophoric uranium hydrides during storage. A multi-laboratory EMSP project was designed to deliver information that could be used to make rational decisions about the safety and treatment issues associated with dry storage of spent fuel.
- Acceptance of long-term storage of fuel rods in a geological repository will require knowledge of the potential for release of radionuclides, and two EMSP projects have explored potential release mechanisms.

# Technical Summary and Progress

*Passivation of Spent Fuel Elements.* Extended storage of spent nuclear fuel in water has caused some of the fuel elements to degrade, and the uranium in degraded elements can react with water to form uranium hydride. When the elements are removed from water storage and exposed to air, the uranium hydride can react very rapidly with the oxygen in air. By passing an inert gas containing a small amount of oxygen over the fuel elements, they can be passivated by slowly forming oxide layers that will not react further upon exposure to air. The goal of the University of Idaho/Clarksean/INEEL/Ohio State University project (60144) is to develop flow visualization methods and reliable predictive techniques for the passivation treatment operations. They have developed an experimental apparatus to simulate reactive flow patterns and have shown that reactions may decrease the likelihood that all corroded areas will be properly treated. Other experiments have been used to obtain fundamental measurements of the velocity and turbulence fields in idealizations of fuel canisters. Various turbulence models were utilized to model the pipe flow in support of the experimental work.

*Processes Relevant to Dry Storage of Spent Nuclear Fuels.* A PNNL/BNL/Rutgers University project (60392) addresses several science needs for the Spent Nuclear Fuel program: (1) stabilization of spent nuclear fuel, (2) characterization of spent nuclear fuel, (3) development of methods to remove moisture without damage to fuel elements, and (4) characterization of corrosion for fuel elements. A detailed study of the interaction of water vapor with uranium dioxide at room temperatures indicated that adsorbed water is completely dissociated and that oxygen atoms are incorporated into the surface. Gamma radiation-induced degradation of water on a variety of oxide particle/water interfaces was studied. It was found that zirconia increases the hydrogen yield relative to pure gas-phase water, whereas other oxides had very little effect or even inhibited the formation of hydrogen. Zirconia films are important to the integrity of zirconium-alloy fuel-rod cladding, and the breakdown of such films was studied under extreme radiation conditions to clarify the mechanism of oxygen removal from such surfaces.

*Direct Imaging of Spent Nuclear Fuels and Fissile Materials.* A Naval Research Laboratory/LBNL project (60141) is directed toward the application of high-resolution, position-sensitive germanium gamma-ray detectors for direct imaging of spent nuclear fuels and fissile materials. The project is developing an array of double-sided germanium strip detectors, and a prototype system was developed using existing germanium detector technology. A double-sided orthogonal strip germanium detector was fabricated for the first time with an amorphous contact process for the purpose of improving imaging capabilities. The image capabilities of the system will be tested with simple uranium and thorium pieces, and then field tests will be conducted with plutonium buttons and spent fuel rods. The unique aspect of the system is that it will not only possess imaging capabilities but also high-resolution gamma spectroscopy for isotope identification.

*Potential Reactions of Uranium Oxides in a Repository.* A University of Michigan project (59849) is focused on developing models for the reactions of uranium dioxide in spent nuclear fuel that is stored in a repository, such as Yucca Mountain. The models are based on studies of the long-term corrosion products of naturally occurring uranium oxide minerals under oxidizing conditions. The research has identified likely phases of uranyl compounds that may form, and the group has developed methods for predicting the thermodynamic properties of uranyl phases to enable predictions of species present at equilibrium. The ability of uranyl phases to incorporate key radionuclides has also been studied in order to understand which of them may make important contributions to exposure dose during geologic disposal.

*Effects of Oxidation Reactions on the Release of Radionuclides from Stored Fuel.* In a study related to the previous one, the Notre Dame/ANL/University of Missouri–Rolla project (59960) is also exploring the effects of products of $UO_2$ oxidation on the release of radionuclides. They have determined the crystal structures of several uranyl phases in order to improve understanding of radionuclide incorporation into the phases that can form under repository conditions, and they have conducted both theoretical and experimental investigations of the incorporation of various radioactive products of spent fuel into these new phases. A major thrust of their work has been to synthesize and then characterize a number of new uranyl compounds in order to understand which of these compounds may form over long times. They have also investigated ion exchange and other mechanisms by which some of the radioactive species in spent fuel interact with the uranyl phases so that better estimates can be made for the potential of release of radioactive species from spent fuel stored in a repository.

## Project Teams

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  Lawrence Berkeley National Laboratory
- University of Idaho
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# SUBSURFACE CONTAMINATION

## SUBSURFACE CONTAMINATION IS A DIFFICULT CLEANUP PROBLEM, BUT NEW TECHNOLOGIES CAN SIGNIFICANTLY REDUCE REMEDIATION COSTS

The 1997 EMSP awards that are most closely related to areas of concern to the Subsurface Contaminants Focus Area (SCFA) are described below. The technical summaries are organized according to the five SCFA strategies (Identify, Contain, Remediate, Remove, and Validate) rather than by the current work packages.

Most of the projects in this set deal with identification of specific contaminants or with characterization of the subsurface. The original developers of sensors based on microcantilever technology worked on new applications, such as sensors for selective determination of metals in water with sensitivities as low as parts per trillion. Another group worked on the design of a miniature nuclear magnetic resonance instrument that would be inexpensive enough for field applications. The partitioning of radon between organic liquids and water was being explored as a possible tool for locating organic liquids in the subsurface. Another study was focused on the mobility of the very low amounts of plutonium that have been dispersed in Rocky Flats soils.

Noninvasive geophysical tools for shallow subsurface characterization were being examined by four projects. Techniques under investigation include advanced seismic methods, a very early time electromagnetic system, use of combined seismic and ground penetrating radar data, and electrical conductivity and dielectric permittivity.

The ability of sediments beneath Hanford tanks to immobilize cesium long enough for radiative decay was the subject of a project related to passive containment. Two projects involved bioengineering for remediation efforts. One of these focused on the introduction of genes to enable a radiation-resistant bacterium to detoxify organic pollutants, while the goal of another was to develop transgenic plants that can accumulate specific heavy metals from the soil. Another project involved development of computational methods for optimization of groundwater pump-and-treat systems.

**Seismic Reflection and Ground Penetrating Radar in the Shallow Subsurface**
A University of Kansas project (60199) has shown how shallow, three-component seismic reflection techniques and ground penetrating radar methods can assist in characterizing hydrologic-transport parameters in the shallow subsurface. The group has found that one of the keys to imaging seismic targets that lie within a few meters of the Earth's surface is to position the seismic sensors (geophones) within a few centimeters of each other (photo from Great Bend, Kansas test site).

### PROBLEMS/SOLUTIONS

- Despite numerous developments in the past, improved field instrumentation for characterization and monitoring soils and groundwater are still needed (STCG # ID-S.1.04). An innovative, new sensor array system based on the use of microcantilever sensors is being developed in one EMSP project, and another is designing a miniature nuclear magnetic resonance instrument that will be inexpensive enough for field applications.
- Characterization of the geology of the shallow subsurface and an ability to locate buried objects in the subsurface are critically important capabilities. Several EMSP projects are exploring state-of-the-art geophysical techniques for application to DOE needs.
- As stated in an STCG science need (RL-SS30-S), “Fundamental geochemical and chemical investigations are desired to understand cesium migration in micaceous materials…to design or select appropriate remedial technology for cesium migration mitigation in the Hanford unsaturated zone.” This is precisely the subject of an EMSP research effort that has found that sediment-bound cesium has a low potential for migration.

### ANTICIPATED IMPACT

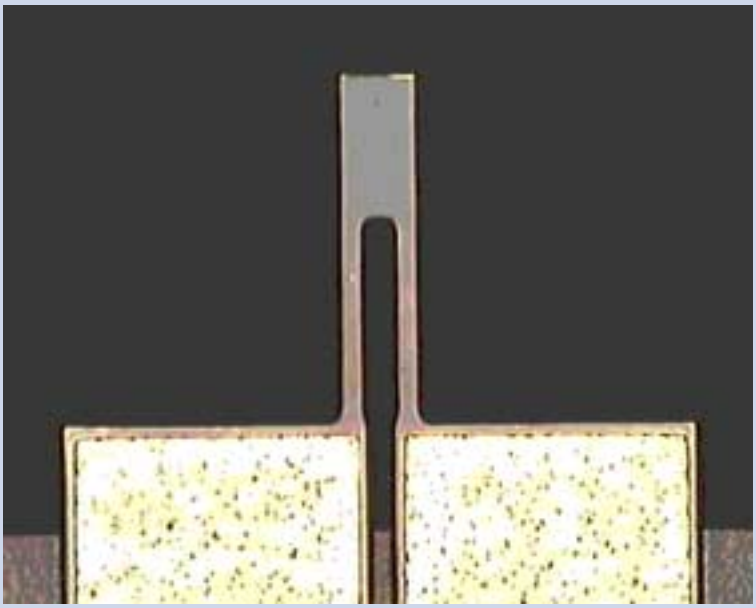
- DOE’s subsurface cleanup challenge includes 475 billion gallons of contaminated groundwater in 5,700 different plumes and 75 million cubic meters of contaminated soil. A recent National Research Council study of *Research Needs in Subsurface Science* concluded that there is sufficient time to do the basic research required to support the development and application of new and improved technologies that could result in large reductions in the cost for remediation.
- An EMSP project has investigated genetic engineering of a radiation resistant bacterium to enable it to degrade several organic pollutants. Bioremediation using these extremely radiation resistant variants in highly contaminated soils could reduce the migration of metals into the environment as well as detoxifying the organic compounds in the wastes.

## Identify – Locate and Quantify Subsurface Contaminants

*Sensor Arrays Based on Microcantilever Technology.* The objective of an ORNL project (60197) is the development of miniature, low-power sensors based on the microcantilever technology that the ORNL group originated. The silicon-based microcantilevers are similar to those used for atomic force microscopy, and changes in cantilever position or vibration frequency can be detected by using reflected laser light. By attaching selective molecular recognition agents onto the cantilevers, the sensors can be made highly selective with sensitivities in the range of parts per trillion. Modified cantilevers for selective determinations of cesium, lead, mercury, chromium, and strontium in groundwater were being developed. Other applications include highly sensitive sensors for changes in pH, sensors for benzene, toluene, and hydrogen, and a novel detector for alpha particles. A future goal is the development of arrays of these miniature sensors for cost-effective, in-situ, real-time characterization of contaminated groundwater or mixed waste sites.

*A Fieldable, Miniature Nuclear Magnetic Resonance Instrument.* The objective of a University of Illinois–Chicago project (60247) is to develop a nuclear magnetic resonance (NMR) spectrometer that is small enough to be held in the palm of a hand and that could be used for in-field characterization of contaminants, process analysis, or even downhole monitoring of groundwater pollutants. NMR spectroscopy is widely used for identification and structural studies of chemical species, but conventional instruments are very large, expensive instruments that cannot be adapted for field use. The main focus of this project has been on a thorough evaluation of the design criteria for a new, miniature instrument that would be inexpensive, fieldable, and have sensitivities of 10 to 100 parts per million for proton-containing molecules. The initial instrument will be designed for proton NMR, but it could be adapted for fluorine-19, phosphorous-31, or carbon-13 NMR.

*Use of Radon Partitioning to Locate Organic Liquids.* Radon is produced by the decay of naturally occurring radium-226, and it occurs in groundwater as a dissolved gas. If the groundwater is in contact with an immiscible organic liquid, then the concentration of radon in the groundwater will be reduced because radon preferentially partitions into organic liquids. The Oregon State University project (60158) is investigating the feasibility of using radon determinations from several groundwater sources in an area to locate organic liquids in the subsurface. Laboratory studies using a physical aquifer model suggested that the technique could detect the presence of an organic liquid. If partition equilibrium were obtained, then the decrease in radon concentrations in groundwater would be dependent upon the partition coefficient and upon the ratio of the volumes of groundwater and organic liquids in contact. However, radon-222 has a half-life of only 3.83 days, so the distribution would be more complex. Initial field tests at a site where perchloroethylene was known to be present were ambiguous.



**Sensor Arrays Based on Microcantilever Technology**
The objective of an Oak Ridge National Laboratory project (60197) is development of miniature, low-power sensors based on the microcantilever technology that the ORNL group originated. Above is an optical image of a 180-microns-long microcantilever sensor.

*Characterization of Plutonium in Rocky Flats Soils.* The goal of a LANL/ORNL project (59996) was to bridge the gap between basic actinide chemistry and the problems that impede characterization and cleanup of plutonium-contaminated sites. Based on isotopic ratio measurements, they determined that non-fallout plutonium (Pu) in Rocky Flats soils was localized directly east of the site and that there was no long-range contamination in other directions. The first definitive spectroscopic data on Pu in an environmental sample showed that Pu in the most concentrated samples was in the form of plutonium dioxide, a highly stable and immobile form. They have also compiled Pu thermodynamic data to obtain a database that is useful for modeling. One objective was to calculate the speciation of Pu(IV) under environmental conditions and to define conditions that may control the release of Pu from the dioxide.

*Advanced Seismic Methods for Shallow Subsurface Characterization.* As described in the Subsurface Contaminants Focus Area's Multi Year Program Plan for FY 2000-2004, DOE sites need better characterization tools to locate contaminants with a minimum of drilling. A Rice University project (60115) is attempting to develop advanced seismic

methods to characterize the subsurface at depths less than 30 meters. Their work has focused on analysis of existing high-resolution data acquired at an open pit copper mine, new data acquisition at an environmental remediation site, and data processing algorithm development. Work at the remediation site, Hill Air Force Base in Utah, has involved characterization of a DNAPL-containing channel in a clay layer. They used three different seismic sources, which provided signals with frequencies from about 30 Hertz to about 300 Hertz. The location and depth of the channel estimated from the seismic data corresponded closely to the assumed location based on available well data.

*Very Early Time Electromagnetic System for Shallow Subsurface Imaging.* The objective of the U. S. Geological Survey/University of Illinois project (60162) is to enhance a very-early-time electromagnetic (VETEM) system for imaging of the shallow subsurface in media where ground penetrating radar (GPR) provides insufficient penetration and time domain electromagnetic systems yield insufficient resolution. The system has been tested at the Cold Test Pit and at Pits 4, 9, and 10 at INEEL and also at Denver over a former munitions factory. The VETEM images at the munitions site were better than any that have been produced by GPR or any of the commercial electromagnetic systems that had been used previously. The INEEL trials demonstrated the ability to delineate lateral conductivity changes and buried conductive objects as well as an ability to discriminate between anomalies caused by highly conductive materials and more mixed materials.

*Use of Seismic Reflection and Ground Penetrating Radar in the Shallow Subsurface.* The goal of a University of Kansas/SUNY-Binghamton project (60199) was to show how shallow, three-component seismic reflection techniques along with GPR methods could assist in characterizing hydrologic-transport parameters in the shallow subsurface. Shallow seismic reflection methods have usually been capable of imaging the subsurface at depths from 2 to 30 meters. By modifying the field layout of the geophones and using an alternative seismic source, this group was able to image the subsurface at depths of 0.6 to 2.1 meters using seismic reflections. They were also able to image the water table at a depth of about 2 meters using GPR. Other work consisted of applying the combined seismic and GPR techniques to characterization of the cone of depression around active irrigation wells.

### Project Teams

**Lead Principal Investigator (Award Number)**

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  Pacific Northwest National Laboratory
- Los Alamos National Laboratory
  PI: Mary P. Neu (59996)
  Oak Ridge National Laboratory
- University of Vermont
  PI: George F. Pinder (60069)
- Rice University
  PI: Alan R. Levander (60115)
- Oregon State University
  PI: Lewis Semprini (60158)
- U.S. Geological Survey–Denver
  PI: David L. Wright (60162)
  University of Illinois
- Oak Ridge National Laboratory
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- University of Kansas
  PI: Don Steeples (60199)
  State University of New York–Binghamton
- University of Illinois–Chicago
  PI: Gennady Friedman (60247)
- Dartmouth College
  PI: Mary Lou Guerinot (60271)
  University of Missouri–Columbia
- Lawrence Berkeley National Laboratory
  PI: Ki Ha Lee (60328)
  University of California–Berkeley
- Pacific Northwest National Laboratory
  PI: John M. Zachara (60355)
  Savannah River Ecology Laboratory

*Electrical Conductivity and Dielectric Permittivity of the Shallow Subsurface.* Another subsurface imaging technique is being explored by the LBNL/UC–Berkeley project (60328). They are developing a noninvasive method for accurately imaging the electrical conductivity and dielectric permittivity of the shallow subsurface using high frequency electromagnetic impedance measurements. Initial field measurements were done at a site that was relatively conductive, so the electric field measurements were difficult to make. High-frequency impedance data were also made at two sites with a more resistive environment. The latter sites were expected to have parameters similar to those that would be found for landfill caps. The general applicability of the technique had not yet been demonstrated but was to be discussed in the final report of the project.

### Contain – Contain or Stabilize Mobile Contaminants

*Mobility of Cesium in Hanford Sediments beneath Leaking Tanks.* About a million gallons of waste containing a million curies of radiation, mostly due to cesium-137, has leaked into the subsurface underneath some of the Hanford tanks. If the cesium is strongly adsorbed onto minerals for sufficient time to allow full decay, then there will be no reason to undertake massively expensive remediation efforts to recover the cesium. A PNNL/Savannah River Ecology Laboratory project (60355) has shown that the cesium migration depth is strongly controlled by the sodium ion concentration, and their studies of competitive binding of cesium, sodium, potassium, and calcium ions provide the basis for improved models of cesium adsorption onto Hanford sediments. The results have indicated that sediment-bound cesium is fixed and not available for further migration, and their work should allow firm guidance on whether cesium beneath the tanks can be left in place without remediation efforts.

## Remediate – In-Situ Treatment of Subsurface Contaminants

*Remediation of Organic Compounds Using Radiation-Resistant Bacteria.* Numerous microorganisms have been found to have the ability to degrade a variety of organic pollutants, but generally they are sensitive to radiation and do not function in wastes containing both organic materials and radionuclides or heavy metals. The bacterium *Deinococcus radiodurans* is the most radiation resistant organism known, but it does not detoxify organic pollutants. A Uniformed Services University/ University of Minnesota/PNNL project (59786) has used genetic engineering techniques to enable *D. radiodurans* variants to detoxify various organic compounds. They constructed a recombinant *D. radiodurans* that expresses toluene dioxygenase, and this bacterium has the ability to oxidize toluene and several other compounds in a highly irradiating environment. They have also worked on constructing variants for the degradation of halogenated aromatic compounds and several other common pollutants. In addition, they have developed a strain that can metabolize toluene or chlorobenzene while at the same time reducing toxic ionic mercury to elemental mercury.

*Development of Transgenic Plants for Remediation of Metals.* It is well known that several plant species may be used for metal ion uptake from contaminated soils, but basic information on the molecular biology of metal ion transport is required to optimize the design of plants for metal remediation. A Dartmouth College/University of Missouri project (60271) is focused on the determination of the role of certain genes that produce metal-transporter proteins as well as identifying details of the protein structures that are responsible for the metal-ion affinity. One goal of the work is to develop transgenic plants that are able to accumulate specific heavy metals. Another goal is to develop a better understanding of metal ion uptake in humans so that more reliable risk assessments for ingested metals can be determined.

## Remove – Extract Contaminants from the Subsurface

*Optimization of Groundwater Pump-and-Treat Systems.* The development of computational methods for the optimization of groundwater pump-and-treat remediation systems is the objective of a University of Vermont project (60069). The proposed methodology will use a groundwater flow and transport model to determine the optimal locations and pumping rates for groundwater wells. The solution of the model is dependent upon the assumed hydraulic conductivity of the aquifer, and the work in this project incorporates uncertainty in the conductivity in the optimization problem. The objective of the research is to provide a least-cost design that will avoid the risk associated with designing a system modeled using uncertain hydrogeologic information.

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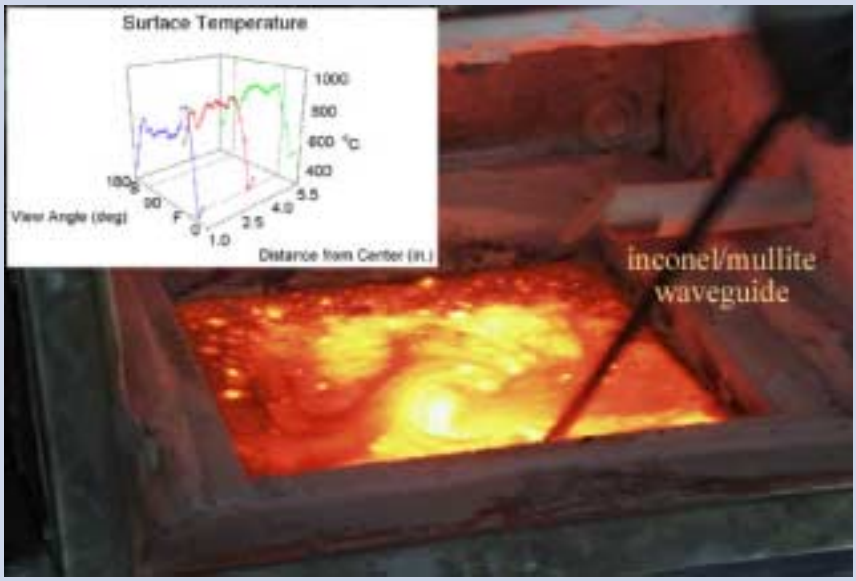
# ANALYTICAL CHEMISTRY AND INSTRUMENTATION

## SEVERAL INNOVATIVE NEW ANALYTICAL TECHNIQUES ARE BEING EXPLORED FOR CHARACTERIZATIONS OF CONTAMINATED SURFACES AND HIGH-LEVEL WASTES

There were three analytical chemistry projects awarded in 1998 whose focus was of primary interest to deactivation and decommissioning (D&D) activities. One is exploring the development of a portable radionuclide analyzer using capillary electrophoresis, and two microchip systems have been produced for detection by absorbance and fluorescence. Another sensor is based on a periodic array of colloidal particles that are polymerized into a gel such that the color of the diffracted light is affected by analytes diffusing into the gel. A third project is exploring the use of terahertz time-domain spectroscopy and imaging for real-time identification of asbestos as well as an unrelated development of gamma spectroscopy methods for determining radioactive depth profiles of radionuclides in surfaces.

Four EMSP projects were focused on characterization issues for high-level tank wastes. The potential for use of microcantilevers for sensing applications was first explored at Oak Ridge National Laboratory, and the goal of an EMSP project in this area is to develop sensors that can be used to detect target chemicals in a mixture, radiation emitted by radioactive materials, and absorption of photons of specific wavelengths by target chemicals. Another sensor project is investigating use of arrays of semiconducting oxide films whose conductivity changes as gases are adsorbed onto the films. Laser vaporization of tank-waste samples for mass spectrometry is attractive because it requires tiny quantities of material. One project has demonstrated calibrated identification of organics with attomolar sensitivity from picogram quantities of waste simulant. The goal of another university-national laboratory group is developing new diagnostic tools for real-time characterization of molten glass.




**Real-Time Characterization of Molten Glass**
An MIT project (65435) is developing new diagnostic tools for enhancing production of optimal glass composition in vitrification facilities through real-time characterization of molten glass. Above: Millimeter-wave pyrometer surface temperature scans of an Idaho National Engineering and Environmental Laboratory surrogate waste glass in the EV-16 melter at Clemson University.

### PROBLEMS/SOLUTIONS

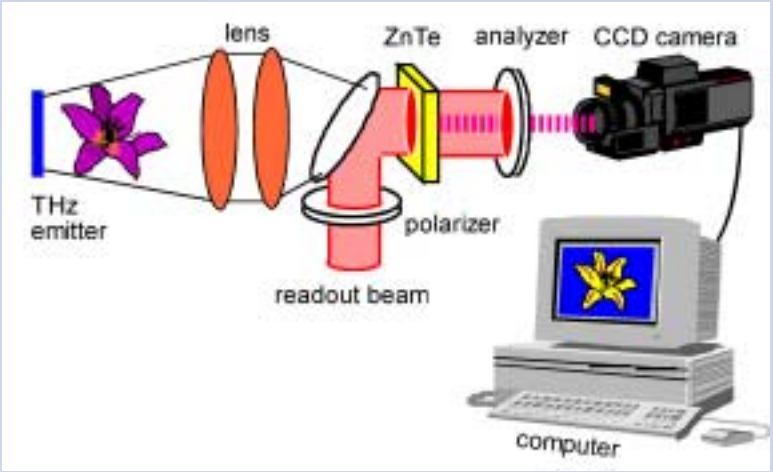
- Conventional analytical methods used to characterize contaminants on surfaces of materials are often expensive and slow because they require taking the samples to a laboratory. EMSP projects related to characterizing such surfaces involve potential applications of state-of-the-art techniques such as a portable radionuclide analyzer using capillary electrophoresis on a chip, color-changing sensors made from polymerized crystalline colloidal arrays, and identification of asbestos using terahertz spectroscopy.
- Semiconducting oxide thin films can be used as robust sensing materials because their conductivity changes as gases are adsorbed onto their surfaces. However, a single sensor cannot be used with most gas mixtures. To monitor analytes within mixtures, a variety of oxide films are incorporated into micromachined array platforms to form multiple microsensing elements that include local temperature control. The combination of materials sets and temperature variation provides a basis for developing a range of low power, inexpensive arrays for gas monitoring.

### ANTICIPATED IMPACT

- As stated in a recent National Research Council report, “the development of minimally- and noninvasive technologies to characterize the concentrations of contaminants as a function of depth within concrete” should be a high priority for EMSP, and one EMSP project has been working on obtaining depth profiles using gamma spectroscopy.
- The DOE system stores about 90 million gallons of high-level waste, and the nature of the wastes in different tanks is often diverse. Developing robust analytical methods for such a variety of materials has proved difficult, so explorations of advances in analytical measurement techniques by several EMSP projects may still lead to useful characterization methods.
- Microcantilever sensors were first developed in a DOE laboratory, and an EMSP project is exploring innovative applications as detectors for target chemicals and for detection of radionuclide emissions.

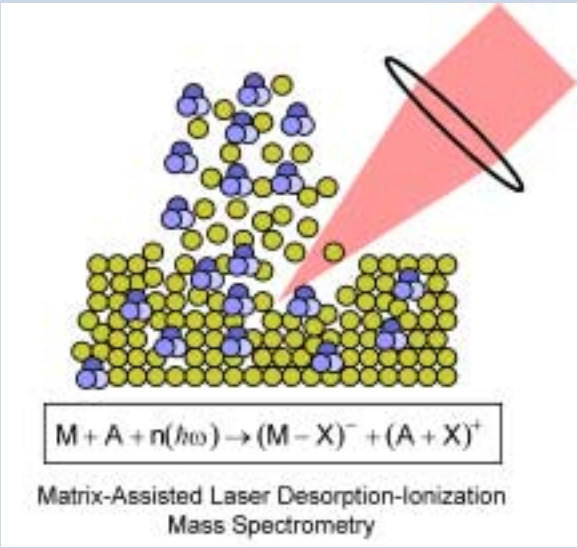
## New Characterization Tools for Deactivation and Decommissioning Projects

*Capillary Electrophoresis Separations on a Chip.* The goal of a Naval Research Laboratory/ Geo-Centers project (64982) is to develop a sensitive, selective, portable radionuclide analyzer. The plan is to use derivatized macrocycles with high affinities for specific metal ions or a small class of metal ions in conjunction with capillary electrophoresis separations on a microchip. Two microchip systems have been produced, one for detection by absorbance and another by fluorescence. A rhodamine tagged calixarene has enormous selectivity for uranyl ions over other metals, and the metal complex could be separated on the microchip in less than 45 seconds from the free ligand and detected by fluorescence. Absorbance detection was used for a commercial dye, Arsenazo III, which forms stable complexes with lanthanides and actinides but not with alkali or alkaline earth ions. By adjusting separation conditions, the dye can be used for a simple, highly selective and sensitive detection of uranium with a detection limit of 27 parts per billion (ppb). High-resolution separation and detection of seven common transition metals in the high ppb range was achieved with another commercial dye, and the analysis was done in less than a minute.




**D&D Applications of Terahertz Spectroscopy**
One of the objectives of a Rensselaer project (65004) is to develop methods for identifying asbestos in real-time in the field using THz time-domain spectroscopy and imaging. Above: Setup for the conversion of a THz image into an optical image. The 2-D field distribution in the sensor crystal is converted into a 2-D optical intensity distribution after the readout beam passes through a crossed analyzer, and a digital CCD camera then records the optical image.

*Chemical Sensing with Polymerized Crystalline Colloidal Arrays.* A University of Pittsburgh project (65001) is exploring applications of a new type of chemical sensing system based on polymerized crystalline colloidal arrays, which were developed by the principal investigator. The sensor is based on a periodic array of colloidal particles that are polymerized into an acrylamide hydrogel. This periodic, colloidal array diffracts light in the visible spectral region. The particles also contain chelating agents to bind metal ions, and when a metal ion diffuses through the gel and binds to the colloid sites, the array is slightly distorted. The resulting change in diffraction wavelength can be used to determine the concentration of the target analyte. This sensing scheme has been tested successfully with arsenous acid, and work is continuing on developing sensing materials for cations of lead, uranium, plutonium, strontium, mercury, cesium, and cobalt, for example.




**Matrix Assisted Laser Desorption and Ionization**
A Vanderbilt University project (65425) has studied matrix-assisted laser desorption and ionization using a tunable, mid-infrared free-electron laser that can be tuned into vibrational bands of sodium nitrate.

*D&D Applications of Terahertz Spectroscopy and Gamma Spectroscopy.* A Rensselaer project (65004) has two objectives: (1) to develop methods for identification of asbestos in real-time in the field using terahertz (THz) time-domain spectroscopy and imaging, and (2) to develop methods for determining radioactive contamination depth profiles in the field using gamma spectroscopy. They developed an experiment on a photoconductive transceiver that combines both generation and detection of radiation in the terahertz region. They have obtained measurements of the transmission of asbestos in the THz or far infrared spectral region, but spectral signatures in the initial region studied were insufficient for identification. The radiological contamination depth profiling studies are based on in-situ gamma spectroscopy and require isotopes that emit two or more gamma rays or have gamma-emitting progeny in secular equilibrium with the parent. The method requires data from a limited number of traditional bore samplings for calibration, and it has been shown to have very good predictions for the depth of point contaminants.

## Characterization of High-Level Tank Wastes

*Microcantilever Sensors.* Microcantilevers have been described as "microscopic diving boards" that project from miniature chips, and inexpensive arrays of these devices can be produced. Their usefulness as sensors is based on the bending of the tip or the change in resonance frequency of an oscillating cantilever due to some stress, such as added mass due to adsorption. The goals of an ORNL/University of Tennessee project (65340) are to develop sensors that can be used to detect simultaneously target chemicals in a mixture, radiation emitted by radioactive materials, and the absorption of photons of specific wavelengths by the target chemicals. They found that thiol-coated devices respond reversibly to the presence of certain phosponate molecules, and that they will also respond to the absorption of light by the adsorbed molecules. In order to increase selectivity, they have investigated applications of a number of chemically selective coatings, such as resins that have high specificity for cesium. Modifications to increase the surface area of the microcantilevers using sol-gels have also been explored, and studies of the interaction of the devices with alpha and beta particles were also planned for future studies.

*Semiconducting Oxide Film Sensors.* A NIST/University of Maryland effort (65421) is directed toward the development of low-cost, reliable sensors for continuous monitoring of gas-phase species. Semiconducting oxide films are deposited onto the elements of micromachined arrays and then electrical conductivity changes are recorded as gases are adsorbed onto the films. Of course, a simple one-parameter measurement cannot be used for multicomponent gases, so a variety of oxide films have been prepared in order to produce arrays of films with different properties. Another feature of the "micro-hotplate" array elements is that they can be individually addressed and rapidly heated so that changes in conductance as a function of temperature can provide additional information. Arrays similar to the microsensor prototypes, but with up to 50 elements, are employed to develop response databases that relate film composition and microstructure to sensing performance for analytes of interest. Chemometric and neural-network modeling is used to analyze the high-information-content data collected with the microsensor arrays for a range of gas-monitoring applications.

*Real-Time Characterization of Molten Glass.* The production of optimal glass composition in vitrification facilities could be enhanced with real-time characterization of molten glass, and the development of new diagnostic tools for this purpose is the goal of an MIT/PNNL/SRTC project (65435). Millimeter-wave measurements of molten glass have been done using waveguides made of inconel and mullite, and techniques for determining temperature, emissivity, viscosity, and density have been explored. A new thermal analysis capability for non-contact molten glass measurements appears possible. Other work has involved measurements of the electrical conductivity of glass melts. An important goal is to correlate the measured physical properties of the molten glass with chemical composition. The final task of this work is to develop a new feedback control strategy for glass melters based on the monitored physical properties of the molten glass and the desired glass product. Higher waste loading would be possible with such a control capability thus lowering waste immobilization costs.

*Matrix Assisted Laser Desorption and Ionization.* Rapid determination of atomic and molecular constituents of high-level waste tanks is a formidable challenge, and laser vaporization of the very tiny sample masses needed for mass spectrometry has promise for these mixtures. A Vanderbilt University/PNNL project (65425) began with studies of matrix-assisted laser desorption and ionization using a tunable, mid-infrared free-electron laser that can be tuned into vibrational bands of sodium nitrate. They have shown that they can detect molecular ions of major organic constituents of tank waste using the sodium nitrate itself as a matrix, and that adducts from the sodium nitrate can be used as an intrinsic internal standard to calibrate the absolute yields of these organics below the ppm level. The maximum sensitivity demonstrated so far is in the few attomole range. Adding a highly absorbing substance to the samples also makes possible efficient ion production by ultraviolet lasers without undue fragmentation. Significant progress has been made in understanding the mechanism of charge generation and transfer during the desorption process, so that the process can be certified.

### Project Teams

**Lead Principal Investigator (Award Number)**

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  PI: George Xu (65004)
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- Vanderbilt University
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  PI: Paul P. Woskov (65435)
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**Office of Science & Technology**
**Office of Environmental Management**
**U.S. Department of Energy**

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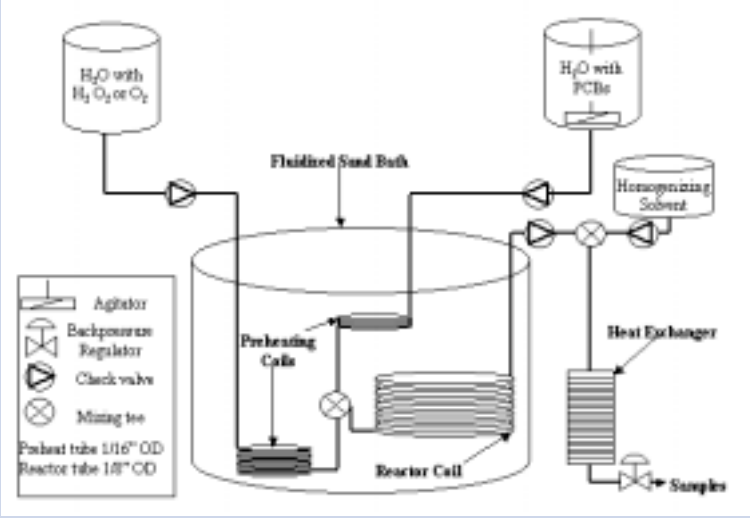
# ENGINEERING SCIENCE AND HYDROGEOLOGY

## MANY PROJECTS INCLUDE NEW METHODS FOR SURFACE DECONTAMINATION AND STUDIES OF HIGH-LEVEL WASTE TREATMENT OPTIONS

Most of the radionuclide contaminants on iron and steel are trapped in the oxide layers on the surface. One of the 1998 Engineering Science projects has explored use of naturally occurring organic species for potential surface-decontamination methods to reclaim the huge inventory of valuable metals in deactivated DOE facilities. PCBs are hazardous contaminants encountered during some D&D operations, so another EMSP effort has been directed toward methods to destroy PCBs without the use of solvents that produce secondary wastes. The location, identity, and concentration of radionuclides within contaminated equipment and structures (such as concrete walls) must be known to eliminate the costly need to dispose of the entire structure as radioactive waste. To address this need, another research program has worked to develop gamma-ray detectors with improved image resolution, sensitivity, and specificity.

Aerosols that form during calcining operations, for example, are potentially a major source for release of radioactive materials during high-level waste processing, and this was the impetus for a study to investigate methods for enhancing the collection efficiency for particulates. The formation of gels and unanticipated precipitates during retrieval of wastes from high-level tanks could cause large delays and increases in costs, so another project was designed to perform an extensive modeling study of the interactions between chemical reactions and flow properties during slurry mixing and transfer operations.

The migration patterns of solutions that have leaked from Hanford tanks must be known in order to decide whether enormously expensive remediation efforts are necessary to prevent unacceptable levels of groundwater contamination. Another EMSP-funded group is using combinations of laboratory and field experiments along with numerical modeling studies to explore this issue.




**Polychlorinated Biphenyl (PCB) Decontamination**
A University of South Carolina, Clemson University, and Savannah River Site project (64979) is investigating a combined extraction and destruction process for decontamination of PCB-contaminated materials at DOE sites. Above: The supercritical water oxidation test stand at Clemson University is being used to determine kinetics for the destruction of chlorinated aromatics and PCBs.

### PROBLEMS/SOLUTIONS

- Most of the current methods for destroying PCBs create some form of secondary waste. Reactions of PCBs in supercritical fluid carbon dioxide or water may provide an alternative treatment technology that uses no hazardous solvents.
- If equipment and building materials have been subjected to radionuclide contamination, the entire structure must be treated as radioactive waste during demolition. However, only partial removal may be necessary if the contamination can be accurately located and identified. Gamma-ray detectors with enhanced image resolution, sensitivity, and specificity are being developed for this purpose.
- Aerosols that form during some processes for treating high-level wastes present a potential source of release of radioactive materials into the environment. Increasing the size of the particulates results in increased particulate collection efficiency, so one project has explored electrical and acoustic methods to cause aerosol particles to coalesce.

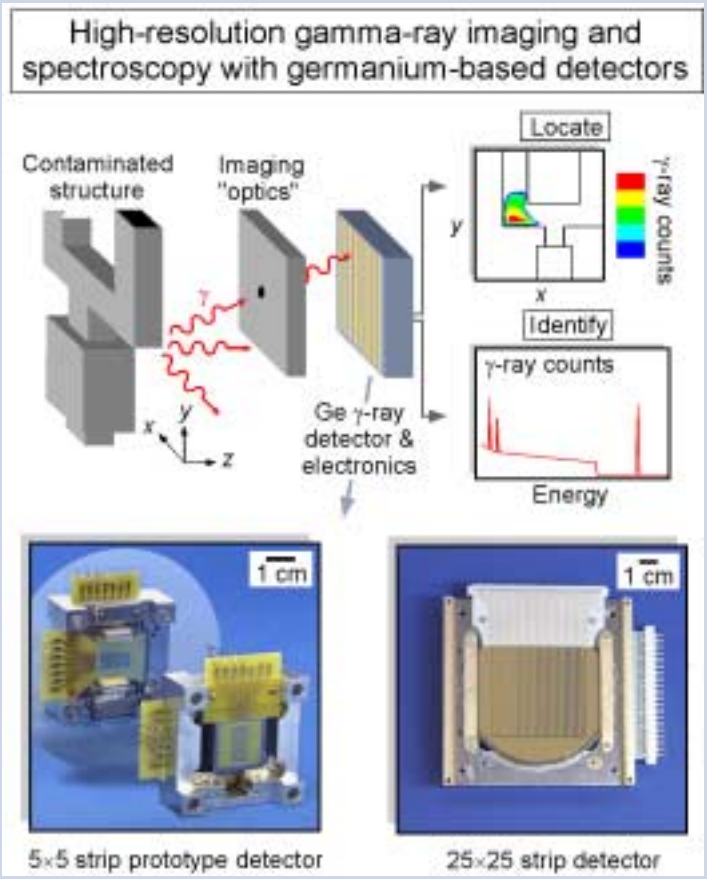
### ANTICIPATED IMPACT

- There are approximately 180,000 metric tons of metal associated with nuclear facilities that are to be decommissioned. The surface oxide layers on iron and steel retain most of the radionuclide contamination, so an effective method for removing these oxide layers would also remove most of the adsorbed radionuclides. One EMSP project is exploring the use of naturally occurring organic chelates for surface decontamination methods that could change the metal from a waste disposal burden into a valuable resource.
- Approximately a million gallons of high-level waste have leaked from Hanford tanks, and retrieval operations could result in additional leakage into the vadose zone. A thorough understanding of the migration of waste species down to the groundwater is crucial for planning future remedial actions, so one EMSP study is exploring the information needed for this problem.

## Engineering Science Projects with D&D Applications

*Materials for Removal of Oxide Layers from Metal Surfaces.* Naturally occurring organic chelates (siderophores) appear to be more effective at oxide dissolution and actinide complexation than synthetic organic materials currently used in decontamination processes. The goal of a PNNL/LBNL/Ohio State University project (64947) is to identify siderophores that are effective at removing the oxide layer from the surface of metals in order to remove radionuclide contamination trapped in the oxide layer. The work uses a combination of molecular, macroscopic, and computational studies to develop structure-function and structure-reactivity relationships. Dissolution studies with hydroxamic acid-type ligands have shown that dissolution rates of iron oxides increase by an order of magnitude as the number of functional groups per ligand molecule increases. Modeling studies led to structure-activity relationships for catecholamide ligands and suggest that this method can be used to screen other similar ligands for selection as candidates for experimental study.

*Polychlorinated Biphenyl (PCB) Decontamination.* Researchers in a project (64979) at the University of South Carolina, Clemson University, and the Savannah River Site are investigating a combined extraction and destruction process for decontamination of PCB-contaminated materials at DOE sites. The work involves studies of extraction with supercritical $CO_2$ or hot water, followed by destruction of the extracted PCBs with either electrochemical or hydrothermal oxidation. The extraction of surrogates for PCBs from a commonly used adsorbent with supercritical $CO_2$ was promising, although not quantitative. A high-pressure reactor for conduction electrochemical super oxide chemistry in high-pressure $CO_2$ is being tested. A continuous-flow supercritical water oxidation apparatus has also been constructed, and screening tests with model contaminants showed promising results using hydrogen peroxide as the oxygen source. Several chlorinated biphenyls will be studied in ongoing work.




**Germanium Gamma-Ray Detectors for Imaging Applications**
A Lawrence Berkeley National Laboratory project (65015) is developing technologies necessary to produce large-area germanium gamma-ray detectors with combined imaging and spectroscopy capabilities superior to that of available technologies. The LBNL group has further refined their existing Ge detector fabrication processes to produce the finely segmented, position-sensitive detectors needed for imaging applications.

*Germanium Gamma-Ray Detectors for Imaging Applications.* The primary objective of an LBNL project (65015) is to develop the technologies necessary to produce large-area germanium (Ge) gamma-ray detectors with combined imaging and spectroscopy capabilities superior to that of presently available technologies. The LBNL group has further refined their existing Ge detector fabrication processes in order to produce the finely segmented, position-sensitive detectors needed for imaging applications. Several detectors have been produced, and a new technique for extracting the depth of gamma-ray interaction within the detector has been demonstrated. This technique will lead to improved image resolution. Furthermore, with these detectors, techniques have been devised to overcome energy resolution degradation effects that can occur in the detectors thereby enhancing detection sensitivity and specificity. Their plan is to combine the newly developed detector technologies with unique electronics also being developed as part of the project in order to produce a prototype instrument for field testing.

## Engineering Science and Hydrogeology Projects for High-Level Waste Remediation

*Improved Aerosol Collection Efficiency.* Aerosols that are formed during calcining, for example, are difficult to contain and present a potential for release of radioactive materials. Because the collection efficiency for most particulate collection technologies increases as the particle size increases, methods for increasing the size of particles in an effluent stream should optimize aerosol capture processes. This is the basis of an ORNL/University of Texas project (65328) that is conducting both theoretical and experimental

studies of electrical and acoustic methods to cause aerosol particles to coalesce to form larger particles. Experimental conditions involving spherical particles falling through a vibrating glycerin bath have been designed to match closely those of acoustic agglomeration of aerosols. An apparatus has been built to study the agglomeration of aerosols in flowing gas streams with applied acoustic and/or electric fields. The experimental results will be compared with simulations for the development and verification of design tools for improved methods.

*Modeling of Chemical Reactions and Flow Properties during Waste Retrieval Operations.* There are interactions between chemical reactions and waste flow properties during slurry mixing for tank waste retrieval operations, and a University of Minnesota/PNNL project (65371) is conducting a numerical modeling study of these processes. This project incorporates previous modeling developments in both groups to support a sound basis for waste retrieval decision making. They have confirmed the importance of accounting for yield strength in non-Newtonian sludge mobilization, and their modeling studies are being used in tank waste mixing test plans at Hanford. Their codes are also being used to examine interactions of chemical and hydrodynamic processes to evaluate how and where the nucleation of unwanted solids may be dynamically induced in waste tanks. Another study involved an evaluation of local areas of unwanted chemical reactions that are not anticipated from small-scale laboratory experiments or modeling with coarse resolution. They are also exploring conditions that could lead to the formation of boehmite, which is a stable hydrate alumina phase that forms a gel and is difficult to retrieve by slurry pumps.

### Project Teams

**Lead Principal Investigator (Award Number)**

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  Lawrence Berkeley National Laboratory
  Ohio State University
- University of South Carolina
  PI: Edward A. Hamilton (64979)
  Clemson University
  Savannah River Technology Center
- Lawrence Berkeley National Laboratory
  PI: Mark Amman (65015)
- Oak Ridge National Laboratory
  PI: David W. DePaoli (65328)
  University of Texas–Austin
- University of Minnesota
  PI: David A. Yuen (65371)
  Pacific Northwest National Laboratory
- Pacific Northwest National Laboratory
  PI: Anderson L. Ward (65410)
  Desert Research Institute
  Oregon State University

*Migration of Materials Leaked from Hanford Tanks.* The migration patterns of the materials that have leaked from Hanford tanks are not well understood, so the goal of a PNNL/Desert Research Institute/Oregon State University project (65410) is to obtain a better understanding of the behavior of dense, high ionic-strength fluids in the vadose zone at the Hanford site. Their study combines laboratory, field, and numerical modeling experiments to study the effects of elevated surface tension, density, and viscosity of highly saline fluids on soil water-retention properties. Using X-ray tomography for laboratory studies of the migration of concentrated sodium nitrate solutions through Hanford sediments, they have shown that the high surface tension of a salt solution results in a higher migration velocity. In addition, as a result of the osmotic gradient, water from surrounding areas migrates into the plume and causes more rapid downward migration. Ongoing field studies are underway to study migration patterns directly. As the salt concentration increases, the surface tension of a solution increases and wettability decreases, so the modeling studies have focused on the consequences of these phenomena, particularly in causing more rapid migration toward groundwater in small columns or fingers.


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**U.S. Department of Energy**

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# INORGANIC AND ACTINIDE CHEMISTRY

## EFFICIENT TREATMENT OF TANK SLUDGES REQUIRES A THOROUGH UNDERSTANDING OF INORGANIC AND ACTINIDE CHEMISTRY UNDER HIGHLY ALKALINE CONDITIONS

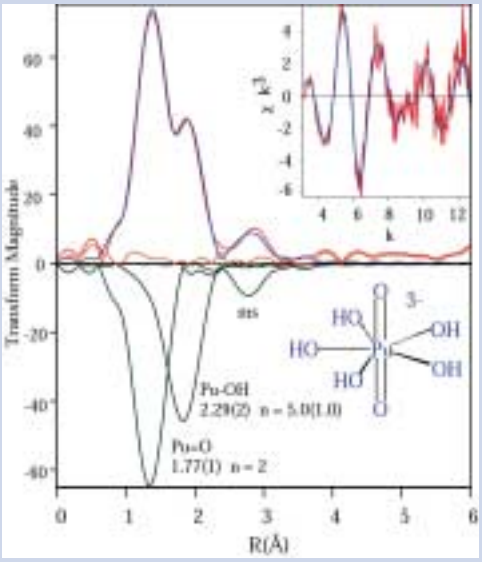
The ideal treatment for all high-level tank wastes would be to remove completely all nonradioactive materials so that a minimum volume of radionuclide-containing materials would need to be immobilized and placed into long-term storage. The projects described below were all designed to explore the inorganic and actinide chemistry of materials in highly alkaline environments similar to those in the tanks or to be used in alkaline scrubs of tank sludges.

It is particularly important that aluminum and chromium compounds be removed from sludges because they interfere with vitrification procedures and greatly increase the total volume and cost for long-term storage. One project is developing data on the solubility of a variety of chromium compounds and on the rates of oxidation of chromium under conditions relevant to high-level waste processing. The interaction of aluminates and uranium compounds is the subject of another study that is directed toward understanding conditions that favor the removal of aluminum from sludges without also dissolving actinide materials.

DOE laboratory researchers have developed self-assembled monolayers on mesoporous supports as a superior method for removing heavy metal ions from solution, and groups at three national labs have cooperated on an EMSP project to extend this technique to enable complete removal of actinides from solution. During this work, they also found a unique method for a simple but nearly quantitative separation of americium from plutonium.

Three EMSP projects involved aspects of the chemistry of actinides in highly alkaline environments. One was a study of the interactions of actinides with aluminates, and another emphasized measurements of the leaching of actinides from sludges during alkaline scrubs. A third effort involved studies of the solubilities of actinides at high temperatures under conditions similar to those in the tank wastes.

**Interaction of Actinides with Aluminate**
A Los Alamos National Laboratory project (65318) is focused on the interaction of actinides with aluminate ions under conditions designed for the pretreatment processes designed to remove aluminum from high-level wastes. At right: X-ray Absorption Fine Structure (XAFS) data (inset) and Fourier Transform for a sample of Pu(VI) in 3.5M hydroxide solution. Data (red) and fit (blue) are shown. XAFS data reveal the formation of the $AnO_2(OH)_5^{3-}$ ions (An = U, Np, Pu), and the molecular structure is indicated in the figure. High aluminate $[Al(OH)_4^-]$ concentrations significantly modify the solution ionic strength and favor the formation of highly charged actinide anions, thereby increasing their solubility under highly alkaline solution conditions.




## PROBLEMS/SOLUTIONS

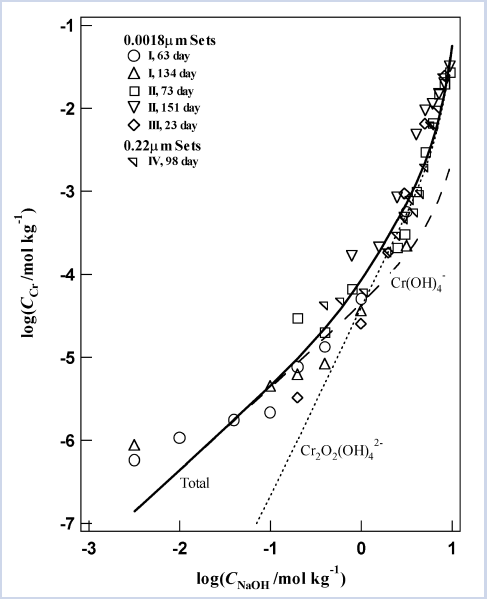
- Chromium compounds are detrimental to vitrification of high-level waste sludges, but current procedures for removing chromium from the sludges are inadequate. An EMSP project was designed to provide fundamental data necessary to develop cost-effective tank waste processing technologies that reduce the amount of chromium in processed waste.
- Although aluminates represent a major component of supernatant liquids in most high-level waste tanks, almost nothing is known about the rates of processes that lead to precipitation or scale formation from supersaturated aluminate solutions. An EMSP project showed that the most stable solid phase of aluminum in alkaline sludges is boehmite, and it is thought that formations of boehmite and sodium phosphate hydrates plugged waste transfer lines during initial waste retrieval and pipeline transfer operations at Hanford.

## ANTICIPATED IMPACT

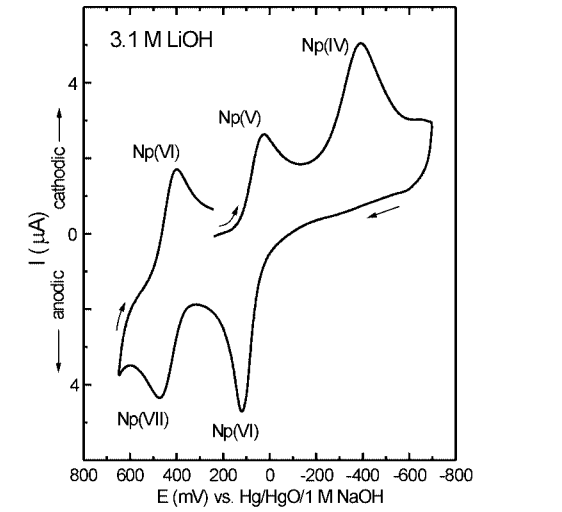
- Separation of the major nonradioactive components from actinides and other radionuclides in high-level tank waste sludge can greatly reduce the costs for immobilization of the radionuclides. The current inability to anticipate the behavior of plutonium and other actinides under the proposed sludge washing conditions must be overcome to reduce the volume of high-level waste in long-term storage, and three EMSP actinide chemistry projects are devoted to providing this information.
- Sorbents with high capacities for removing actinides from solution were prepared in an EMSP project using a unique method for binding ligands to mesoporous ceramics with high surface areas. Separation of plutonium from americium at low concentrations is a critical need for the final disposition of high-level waste, and a selective sorbent material prepared in this project provides a simple and unprecedented capability for achieving this separation.

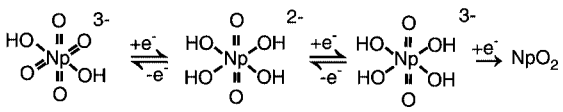
## Chemistry of Inorganic Materials in Tank Sludges

*Chromium Chemistry.* There is a lack of fundamental information about chromium (Cr) chemistry under conditions similar to those in the high-level waste tanks, and procedures for removing Cr from tank sludges either remove too little Cr or too much of the actinides. A PNNL/LBNL/Washington State University project (65368) is developing data on the solubility of Cr(III) compounds and the rates of oxidation of Cr(III) under conditions relevant to high-level waste processing. They have determined the solubility of amorphous chromium(III) hydroxide in different electrolytes (NaOH, $NaNO_3$) and have developed a thermodynamic model to predict Cr(III) behavior in tank solutions dominated by these electrolytes. The Cr concentrations predicted by this model were in close agreement with the observed concentrations in caustic leachates of tank sludges. They have found that the rate of oxidation of Cr(III), in addition to other factors, is highly dependent on the nature and concentration of the soluble Cr(III) species. Additional data on the effect of other electrolytes, Cr(III) solid phases, and oxidants will be obtained to develop reliable methodology to remove Cr from sludges.




**Chemistry of Inorganic Materials in Tank Sludges**
A Pacific Northwest National Laboratory project (65368) is developing data on the solubility of Cr(III) compounds and rates of oxidation of Cr(III) under conditions relevant to high-level waste processing. Chart at left: Solubility of $Cr(OH)_3$(am) in NaOH solutions at different equilibration periods. Lines represent predicted concentrations using the thermodynamic model developed in this project. Solid line represents total chromium concentrations; other lines represent concentrations of species as marked in the figure.




**Leaching of Actinides from Sludges**
Work in an Argonne National Laboratory project (65398) emphasized the leaching of actinides from materials that simulated the sludges formed from three of the plutonium purification processes used at Hanford and the speciation of actinides in concentrated alkali. Above: Cyclic voltammogram of Np species in 3.0 M LiOH indicating electrochemical reversibility of the Np(V)-Np(VI) couple, pseudo-reversibility of the Np(VI)-Np(VII) couple, and irreversibility of the Np(V)-Np(IV) couple. Combined with the results of spectrophotometry, the dominant hydrolytic species of Np(V), Np(VI), and Np(VII) are most probably the (nearly) isostructural octahedral species shown.

*Aluminum Chemistry.* Aluminum-containing phases are the most prevalent solids that can appear or disappear during high-level waste processing, and the unexpected formation of precipitates could be a serious problem during remediation activities. So the goals of a PNNL/Princeton/SRTC project (65411) were to identify aluminum-containing phases and to predict the conditions under which they can form. The two most widely observed phases of aluminum in alkaline wastes are gibbsite and boehmite, and work in this project has concluded that in alkaline solutions boehmite is always the stable phase, and that gibbsite tends to transform to boehmite. The mechanism of the transformation can vary with different circumstances, but the existence of high concentrations of nitrate salts, for example, delayed but did not stop the transformation to boehmite. They have also found that the presence of silicate has a large effect on the activities of aluminum hydroxide and that short-chain carboxylic acids have a big effect on aluminum oxyhydroxides in solution.

## Chemistry of Actinides in Tank Wastes

*High-Capacity Sorbent Materials to Remove Actinides from Solution.* Low concentrations of actinides in the complex aqueous solutions in high-level tank waste or in the solutions from sludge washing most likely cannot be avoided, so the objective of a PNNL/ANL/LBNL project (65370) is to prepare high-efficiency, high-capacity sorbent materials for selectively removing actinides from these solutions. They have used supercritical carbon dioxide or nitrogen as the reaction medium for the deposition of self-assembled silane monolayers in mesoporous ceramic materials with the highest population density ever reported for such systems, and this procedure can be extended with a virtually limitless number of different ligands. Preliminary screening studies of these materials with lanthanides showed very high affinities for the metal ions with reaction times of less than a minute. Systems with high affinities for plutonium

have been found, and one system has a high affinity for plutonium but almost none for americium at lower pHs, so this system may provide a simple method for separation of these two actinides in solution. Materials for the separation of all of the actinides from thorium through americium were being explored, and systems with cationic ligands on the mesoporous support were being investigated as agents for removing pertechnetate from solution.

*Interaction of Actinides with Aluminate.* The chemical forms of uranium and other actinides in highly alkaline wastes are not well understood. A LANL/Russian Institute of Physical Chemistry project (65318) is focused on the interaction of actinides with aluminate ions under the conditions designed for the pretreatment processes designed to remove aluminum from high-level wastes. The solubility of uranyl species was found to increase with increasing aluminate concentration, but the cause was indirect rather than by formation of an aluminate-uranyl complex. They have also found changes in aluminum chemistry when uranium is present, including precipitation reactions that do not occur in the absence of the uranyl species. Similar studies are underway to investigate plutonium chemistry under highly alkaline conditions, and results of this study will assist the development of pretreatment operations.

*Effects of Temperature and Electrolytes on Actinide Speciation.* Actinide speciation in high-level wastes is also the subject of a Washington State University/LBNL/University of Idaho project (65352), which is focused on developing a thermodynamic database for complexes of plutonium and other actinides in alkaline systems with elevated temperatures and high electrolyte concentrations. Studies of the solubility of lanthanides and actinides have been conducted over a wide temperature range (30° to 290°C), and their results enable the determination of stability constants for complexation with a number of inorganic ligands under alkaline conditions. Studies of complexes of trivalent species with acetate showed unexpected increases in the formation constants of 1:2 and 1:3 complexes with increasing temperatures. Thus, extrapolation of data from room temperatures may not properly predict the chemistry at higher temperatures, so more experimental measurements are being done to extend existing thermodynamic models.

*Leaching of Actinides from Sludges.* Another study of actinides in tank wastes was pursued by an ANL/LBNL project (65398). This work emphasized the leaching of actinides from materials that simulated the sludges formed from three of the plutonium purification processes used at Hanford and the speciation of actinides in concentrated alkali. The sludges were spiked with tracer concentrations of uranium, neptunium, plutonium, and americium, and then subjected to alkaline and exploratory acidic scrubs. Both uranium and neptunium exhibited moderate solubility while americium and plutonium were less soluble, but there was some indication of colloidal transport of plutonium. Actinide solubilization often accompanies dissolution of iron, chromium, and manganese oxides from the sludges. Electrochemical, spectrophotometric, and X-ray techniques have been used to explore the nature of actinide species in highly basic solutions, and they have found, for example, that $NpO_2(OH)_4^{3-}$, $NpO_2(OH)_4^{2-}$, and $NpO_4(OH)_2^{3-}$ are the dominant species of neptunium V, VI, and VII in strong base. Additional studies with water-soluble complexing agents were also being done.

## Project Teams

**Lead Principal Investigator (Award Number)**

- Los Alamos National Laboratory
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  Russian Institute of Physical Chemistry
- Washington State University
  PI: Sue B. Clark (65352)
  Lawrence Berkeley National Laboratory
  University of Idaho
- Pacific Northwest National Laboratory
  PI: Dhanpat Rai (65368)
  Lawrence Berkeley National Laboratory
  Washington State University
- Pacific Northwest National Laboratory
  PI: Glen E. Fryxell (65370)
  Argonne National Laboratory
  Lawrence Berkeley National Laboratory
- Argonne National Laboratory
  PI: Kenneth L. Nash (65398)
  Lawrence Berkeley National Laboratory
- Pacific Northwest National Laboratory
  PI: Jun Liu (65411)
  Princeton University
  Savannah River Technology Center


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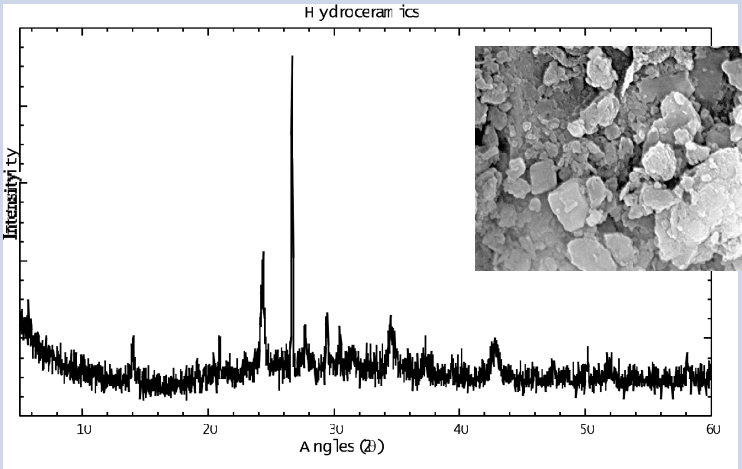
# MATERIALS SCIENCE

## Materials scientists have investigated materials for immobilization of wastes and techniques for decontamination of surfaces

The removal of radionuclide contaminants from surfaces is a high-priority for the Deactivation and Decommissioning Focus Area because otherwise huge volumes of concrete and metals will have to be placed in waste repositories. Several heat treatment techniques have been proposed as alternatives to mechanical methods for removing surface contamination on concrete, so an EMSP project was needed to provide detailed studies of the effect of heating on the engineering properties of concrete. Most of the radionuclide contaminants on metal surfaces are contained in the oxides on the metal surfaces, and one of the studies described here involved an exploration of the efficacy of some simple organic acids for decontamination of metal surfaces.

Three EMSP materials science projects were relevant to high-level tank wastes. One of these investigated thermal reactions of the two organic materials in the tanks that are most likely to be oxidized to form flammable gases. A detailed understanding of this chemistry is important to avoid unexpected gas formation during future mixing operations with materials in the tanks.

The fraction of waste from high-level tanks that can be mixed with glass is typically limited by the formation of spinels, which precipitate to form separate phases and degrade the ability of glass to immobilize the contaminants. An international group of scientists has conducted an extensive examination of the dynamics of spinel formation in molten glass, and they have characterized the role of some minor components in the process. Another project involved the suitability of inexpensively prepared zeolites for immobilization of low-activity wastes that have been calcined, i.e., that contain a large number of different oxides.




**Zeolitization of Tank Wastes**
A Penn State University project (65366) has examined the usefulness of zeolites for immobilizing low-level radioactive waste. Above: X-ray diffractogram of a hydroceramic waste form made from 60 wt% calcine, 40 wt% metakaolinite, and enough water to make a thick paste and cured at 180°C for 7 days. The peaks represent zeolite and quartz that form during the reaction. The insert is a scanning electron micrograph of the waste form meant to illustrate its dense and complex microstructure.

### Problems/Solutions

- DOE facilities have a huge inventory of contaminated metal piping, and as stated in STCG Need ID-7.2.25, "if this metal piping can be effectively decontaminated and reused it will not only reduce the impact on the burial ground, but will save a valuable natural resource." Several EMSP projects are exploring methods for metal surface decontamination, and a project discussed in this fact sheet has studied the effectiveness of certain organic acids for this purpose.
- Zeolites are easy to make and they are good waste forms because they sequester ions within their networks of channels and voids, but little is known about the process of forming zeolites with the complex mixture of oxides that is found in calcined low-activity waste. An EMSP project was designed to provide information on the stability of inexpensive waste forms for immobilization of actual low-level tank wastes.
- The formation of flammable gases in high-level waste tanks is a potential serious safety hazard for tank management. Mechanisms for the generation of flammable gases by thermal reactions of organic complexing agents have been elucidated by an EMSP project.

### Anticipated Impact

- Each 1% increase of the fraction of high-level waste that can be incorporated into glass can save over a half billion dollars of vitrification and disposal costs. Because the formation of spinel precipitates in waste glass melters is the limiting factor for most waste compositions, an EMSP project is aimed at a fundamental understanding of spinel behavior in order to design more efficient vitrification procedures.
- The total area of contaminated concrete in DOE facilities is estimated at about 18,000 acres. Surface heat treatments have been proposed to remove surface contaminants so as to avoid placing all of the concrete into low-level waste repositories, and an EMSP project was designed to improve knowledge of the effects of thermal treatment on the properties of concrete and on radionuclide transport.

# Technical Summary and Progress

## Removal of Radionuclide Surface Contamination

*Effect of Heating on Properties of Concrete.* Techniques proposed for decontaminating concrete surfaces include tools for rapidly heating the surface, such as lasers, plasma torches, or microwaves. An ORNL/Northwestern University project (64896) was designed to study the effect of heating on the engineering properties of concrete as well as on removal of some common radionuclide contaminants. Cured cement powder samples were spiked with short-lived isotopes of cesium, strontium, and cobalt as well as uranium. Heating up to 1300°C resulted in complete vaporization of cesium, but negligible vaporization of the other radionuclides. Extraction of these species with water and dilute acids has also been measured before and after heat treatments. Computations of the mechanics and thermodynamics of concrete during heating have been investigated. Results suggest that conductive heating from the surface produces crumbling of the surface mainly by thermal stresses, but microwave heating produces pore pressures up to 100 atmospheres, which is sufficient to cause spalling.

*Removal of Radionuclides from Metal Surfaces.* A BNL/Stony Brook project (64946) was designed to address fundamental issues related to removal of radionuclide contamination from metal surfaces using hydroxycarboxylic acids, such as citric acid. They have synthesized a number of uranium-containing iron oxide phases and then determined the nature of the association of uranium with the oxides using various spectroscopic techniques. Dilute citric acid solutions were effective in removing uranium from corroded steel coupons that were exposed to uranyl nitrate. Recovery of uranium from the citric acid solutions is necessary to avoid large volumes of secondary waste, and additional work has involved treatment of the waste stream by biodegradation followed by photodegradation and radionuclide recovery.

## High-Level Tank Safety

*Thermal Reactions that Produce Flammable Gases.* Plutonium production at Hanford and Savannah River required large quantities of organic complexing agents that are now stored in high-level waste tanks. These organic materials have been found to degrade to flammable gases, burn in dried wastes, and interfere with radionuclide separations. Several EMSP projects have concentrated on radiolysis of these organic materials, so the objective of a PNNL project (65408) is to study reactions that can occur in the absence of radiation. Of the major complexing agents used at Hanford, only HEDTA and glycolate are readily oxidized by thermal reactions to give flammable gases. The oxidizing agents for these reactions are nitrites, and aluminate ions or other aluminum species are the catalysis, but this work has shown that previously accepted mechanisms for the reactions were not correct. New mechanisms for oxidation of glycolate, HEDTA, and related structures are being explored.

## Immobilization of Tank Wastes

*Formation of Spinels in Molten Glass.* For most Hanford and Savannah River waste streams, the formation of spinels is the limiting factor for the fraction of waste in glass melters. So the objective of a PNNL/Czech Academy of Sciences/Glass Services project (65422) is to develop a basic understanding of the dynamics of spinel formation and motion in molten glass so that waste loading can be maximized. They have developed a mathematical model describing the electric, temperature, and velocity fields in a melter, a model of spinel settling in glass melt, and a physical model to verify the results of the mathematical models. They have found that spinel crystals form during the initial melting stages, dissolve during the final stages of glass formation, and then form again when the temperature drops below the liquidus temperature. In addition to the major spinel-forming nickel, chromium, iron, and manganese oxides, the concentration of some minor components, such as ruthenium and silver oxides, can affect the number, density, and size of spinel crystals.

*Zeolitization of Tank Wastes.* Zeolites have well-known properties and are often used in the manufacturing and nuclear industries for absorption and immobilization of small and large ions. A new process has been developed in which a hard, ceramic-like material called hydroceramic that contains zeolites is prepared from a mixture of metakaolinite and calcined sodium-bearing tank waste. A Penn State University/SRTC project (65366) has examined the usefulness of these materials for immobilizing low-level radioactive waste. Experiments have been performed to determine the conditions needed to maximize the zeolitization process. Various proportions of metakaolinite, calcined waste, and water were cured as a function of time and temperature. Very encouraging results have been obtained in leach tests with these hydroceramics, sometimes exceeding the leach-safe characteristics of high-level waste glass. Hydroceramics appear to offer a viable alternative to vitrification at substantial savings in cost.

### Project Teams

**Lead Principal Investigator (Award Number)**

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- Brookhaven National Laboratory
  PI: A. J. Francis (64946)
  State University of New York–Stony Brook
- Pennsylvania State University
  PI: Michael Grutzeck (65366)
  Savannah River Technology Center
- Pacific Northwest National Laboratory
  PI: Donald M. Camaioni (65408)
- Pacific Northwest National Laboratory
  PI: Pavel R. Hrma (65422)
  Czech Academy of Sciences
  Glass Service, Ltd. (Czech Republic)

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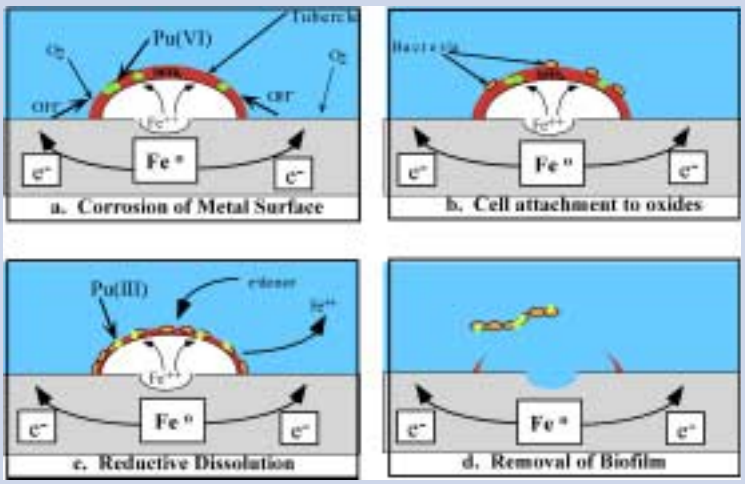
# SEPARATIONS CHEMISTRY

## Advances in separations chemistry could assist in the reclamation of contaminated metals valued at a billion dollars

Removal of contaminants from surfaces is essential if enormous quantities of metals and concrete are not to be placed in repositories, but many possible surface cleaning procedures generate secondary wastes. Two EMSP projects investigated possible uses of high-pressure carbon dioxide as the solvent for surface cleaning procedures in order to avoid other more hazardous solvents. Two groups explored bioremediation for cleaning metal surfaces. One of these investigated the use of polysaccarides produced by algae for the removal of uranium and other heavy metals from steel surfaces. The other investigated the use of iron-reducing bacteria to remove the oxide coating from steel or iron surfaces and thereby also removed adsorbed radionuclides. Another effort was directed toward the use of surfactants for removing oil from metal surfaces, and their work led to development of a surfactant that removed oil much faster than the commercially available materials.

Most of the mass of the materials in the high-level waste tanks is composed of nonradioactive materials, so separations that minimize the volume of materials that need to be stored as high-level waste are a high priority. One exploratory study involved the potential use of crown ethers for removal of cesium with the use of supercritical fluids so as to avoid the use of undesirable organic solvents. Another project investigated some remarkable, but inexpensive, metal oxide clusters for the formation of actinide complexes that could be used directly in vitrification procedures. The use of a new class of ion exchangers was investigated for potential removal of pertechnetate, particularly from dilute solutions. The ion-exchangers use electrically induced charges to expel the sorbed ion rather than conventional chemical eluents. Finally, a unique research program developed a liquid-liquid extraction procedure that could be used to recycle sodium hydroxide in high-level waste tanks.




**Iron-Reducing Bacteria for Surface Decontamination**
This figure, provided by a Pacific Northwest National Laboratory project (64931), illustrates a conceptual model of a potential biological decontamination application using iron reducing bacteria. In such an application, corroding metal surfaces accumulate actinides and other cationic contaminants (a). Iron reducing bacteria attach to and colonize the iron oxide corrosion (b). The bacteria enzymatically reduce and dissolve the oxide layer and reduce actinides that become incorporated into microbial biomass (c). The bacteria with attendant actinides are selectively released by nutrient limitation, enzymatic digest, or mild chemical treatment, from the surface and then collected for disposal (d).

### Problems/Solutions

- High-level waste tanks contain high concentrations of sodium hydroxide, but more will be required for retrieval and sludge washing tasks. A liquid-liquid extraction technique for recovering sodium hydroxide from concentrated solutions has been developed by an EMSP project, and a patent application has been filed as a first step toward developing this technology for applications to tank wastes.
- Chlorinated hydrocarbons were widely used at DOE sites as cleaning agents, and disposal of these solvents resulted in substantial contamination of the subsurface at those sites. Researchers in an EMSP project investigated surfactants for removing oil from surfaces, and they found a simple modification to a commercial surfactant that reduced the time to remove oil by two orders of magnitude.

### Anticipated Impact

- Current technologies for removal of radionuclide contaminants from metal surfaces are costly and produce large volumes of secondary waste, so metals that may be worth a billion dollars could be disposed of as radioactive waste. Several EMSP projects have explored both chemical and bioremediation methods for removing the oxide coating on steel and iron surfaces, thereby removing the contaminants that were adsorbed into the oxide surface layers.
- As described in Science Need S-WT-09-01, effective separation of intensely radioactive cesium and strontium and long-lived components (technetium and transuranic) from high-level waste tanks could greatly reduce disposal costs. An EMSP project investigated the use of transition metal oxide clusters for actinide separations, and this work may provide a new route to not only remove actinides from other wastes but also provide a host that can be used directly for encapsulation in glass.

# Technical Summary and Progress

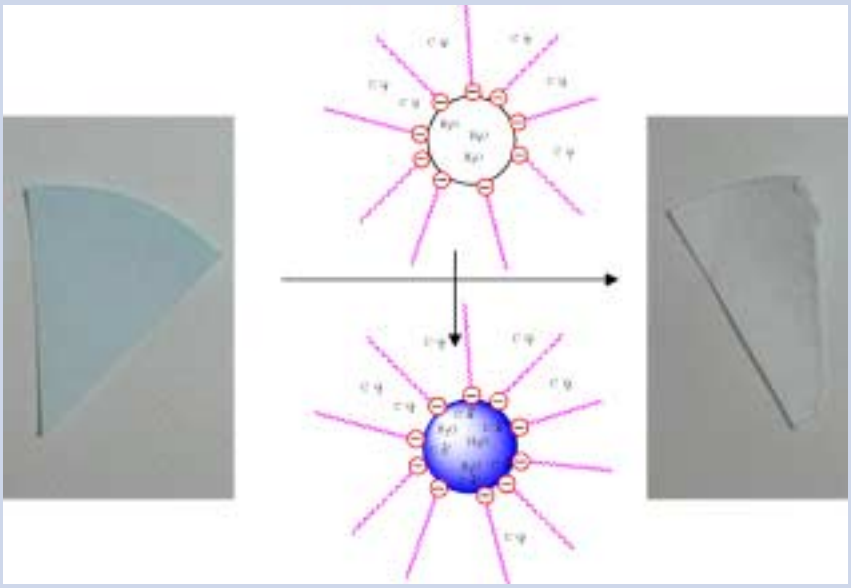
## Decontamination of Surfaces

*Micelles in Supercritical Carbon Dioxide for Extraction of Actinides.* A LANL research program (64865) is investigating micelle formation in supercritical carbon dioxide ($scCO_2$) for use in extraction of actinides and other metals from surfaces. The surfactants are based on perfluoropolyethers, and chelating groups included a carboxylic acid, fluorinated amides, and alkyl phosphates. Soluble surfactants also form microemulsions with water or aqueous acids, and these systems are used for extraction of metals or metal oxides from surfaces. The micelle-containing $scCO_2$ is able to penetrate pores in surfaces much better than pure water. The metal can then be recovered simply by reducing the pressure, which causes phase separation with the metal in the aqueous phase.

*Ligands Usable in Supercritical Carbon Dioxide for Extraction of Actinides.* The objective of an ANL/Loyola University/ Notre Dame project (64965) is to develop substituted diphosphonic acid ligands that can be used for supercritical carbon dioxide extraction of actinide ions from solid wastes. Although diphosphonic acids are known to be good complexing agents for actinide ions, they tend to have low solubilities in $scCO_2$. The synthetic work in this project has involved derivatives in which silicon-containing groups either serve as the ester function or are attached to the carbon of the diphosphonic acid. They have shown that these more complicated derivatives have similar metal extraction properties to the simpler diphosphonic acids. Unfortunately, the new derivatives did not have sufficient solubility in $scCO_2$, so current work is directed toward the synthesis of additional alkyl- and silicon-based diphosphonic acid derivatives.

*Decontamination Using Biopolymer Solutions.* An objective of an ORNL project (64907) is to develop a fundamental understanding of the important parameters for effective decontamination using aqueous biopolymer solutions. The group has cultivated several varieties of algae to produce biopolymers for removal of hazardous metals from surfaces. They have used both reconstituted biomass and partially purified polysaccharides for their studies, and screening studies using copper and uranyl removal were used to select the most promising materials. They have studied uranium and other heavy metal removal from contaminated steel coupons using quantitative determinations of both surface and solution concentrations of the metals, and they have also tested the gel properties of the materials that are best suited for extended contact with surfaces.

*Iron-Reducing Bacteria for Surface Decontamination.* Another approach to metal surface decontamination is being investigated by a PNNL/Montana State/University of New Hampshire group (64931). Their work is exploring the use of iron-reducing bacteria for dissolving iron oxides and thereby releasing the contaminants in the oxide layer. The project is organized according to four tasks: (1) factors that affect the attachment and release of the bacteria from oxide scale, (2) the effects of iron oxide composition and surface properties on cell attachment and biofilm formation, (3) studies of the reductive dissolution of iron oxide scale in the presence and absence of soluble electron shuttles that can enhance the rate, and (4) determination of the distribution of actinides that are released from the iron oxides. Work has progressed on each of these tasks. One result, for example, has been to show that microbially reduced anthroquinone disulfonate can increase the rate and extent of iron oxide reduction as well as markedly increasing the solubility of plutonium by reduction of Pu(IV) to Pu(III).



**Micelles in Supercritical Carbon Dioxide for Extraction of Actinides**
A Los Alamos National Laboratory project (64865) is investigating micelle formation in supercritical carbon dioxide ($scCO_2$) for use in extraction of actinides and other metals from surfaces.

*Surfactants for Removal of Oil from Surfaces.* An investigation of surface decontamination with aqueous surfactant cleaners is being done by an ORNL/ University of Tennessee team (64912). They have used several types of commercial surfactants to investigate the removal of oil from surfaces and have studied the factors that affect oil droplet detachment from metal surfaces. Their experiments are done with single oil droplets on a stainless steel surface with an apparatus capable of monitoring contact angle evolution, droplet shape, and detachment time. A simple modification that reduces detachment time by two orders of magnitude has been

found and is being tested with a company that produces industrial cleaners. The goal of another part of the work is to design separation systems so that wastes are minimized and useful materials such as the surfactants may be reclaimed for reuse.

### Separation of Components of High-Level Wastes

*Extraction of Sodium Hydroxide for Reuse in Tank Operations.* The major objective of an ORNL/University of North Texas project (65339) is to extract selectively sodium hydroxide from high-level waste in Hanford and Savannah River tanks so that it may be used in subsequent waste retrieval and sludge washing operations. A method being tried is to use a highly fluorinated long-chain alcohol that is weakly acidic and is soluble in a suitable organic solvent but not in water. When the organic solvent containing the alcohol is exposed to a highly alkaline water solution, the acidic alcohol is converted to the sodium salt but remains dissolved in the organic solvent. When the latter solution is stripped with water, the alcohol is regenerated, leaving sodium hydroxide in the water. Synergistic effects in sodium hydroxide separations have been found when extractants, such as crown ethers, are combined with the fluorinated alcohol. The results of structural determinations and extraction experiments are being used to guide the syntheses of new extractants and alcohols to find optimal materials for efficient and economical extractions.

*Crown Ethers for Cesium Removal in Supercritical Fluids.* Certain crown ethers are effective for separation of cesium from high-level waste, but this extraction methodology requires the use of undesirable organic solvents. A University of Idaho/PNNL project (65351) was designed to study the nature of the complexes with cesium in solvents ranging from water to organic solvents to supercritical fluids. Nuclear magnetic resonance (NMR) techniques enabled detailed studies of the cesium species present in chloroform and water in the presence of crown ethers, and techniques were available for doing NMR studies on supercritical carbon dioxide solutions. Unfortunately, it was found that the cesium-crown ether complexes are not soluble in supercritical carbon dioxide, but the use of fluorinated anions was being explored to enhance the solubility.

*Electroactive Ion-Exchange Removal of Pertechnetates.* Removal of pertechnetate anions from high-level wastes is important because technetium has a long half-life and pertechnetates are highly soluble and therefore mobile in the environment. With currently available ion exchange resins for pertechnetate removal, unwanted secondary wastes are generated either because of low capacities or because large volumes of hazardous eluants are required to regenerate the resins. A PNNL/BNL/University of Minnesota project (65409) has investigated electroactive ion exchange materials as an alternative for pertechnetate removal. These materials use electrically induced charges to expel the sorbed ions rather than requiring chemical eluents to exchange them. They have investigated ferrocene-containing polymers and have synthesized materials with higher alkaline stability than commercially available products. These materials still did not have adequate stability, so various other polymers were being synthesized and characterized.

*Metal Oxide Clusters for Actinide Retrieval and Immobilization.* Polyoxoanions (POAs) are transition metal oxide clusters held together by metal-oxygen bonds. An ANL/Hunter College project (65378) was designed to investigate the formation of actinide-POA complexes that could selectively remove actinide ions from solution and then be used directly with glass vitrification to immobilize actinides. They have prepared a variety of lanthanide and actinide complexes and performed detailed structural studies of several of the lanthanide-POA complexes in order to better understand the binding mechanisms. Although $[NaP_5W_{30}O_{110}]^{14-}$ had the remarkable ability to reduce cerium(IV) to form $[CeP_5W_{30}O_{110}]^{12-}$, the reaction with neptunium(IV) resulted in oxidation but not encapsulation of the neptunium. Other complexes, however, were found to stabilize neptunium and uranium solutions against oxidation. A niobium species, $[Nb_6O_{19}]^{8-}$, has been studied because it is stable in highly alkaline solutions. They have examined the solubility of POAs in glass, and initial experiments with lanthanide-containing species suggested that the POA complexes decompose during vitrification with borosilicate glasses. Nonetheless, the decomposition produces a homogeneous mixture in glass, so the POA complexes may provide a useful form for actinide extraction and immobilization.

## Project Teams

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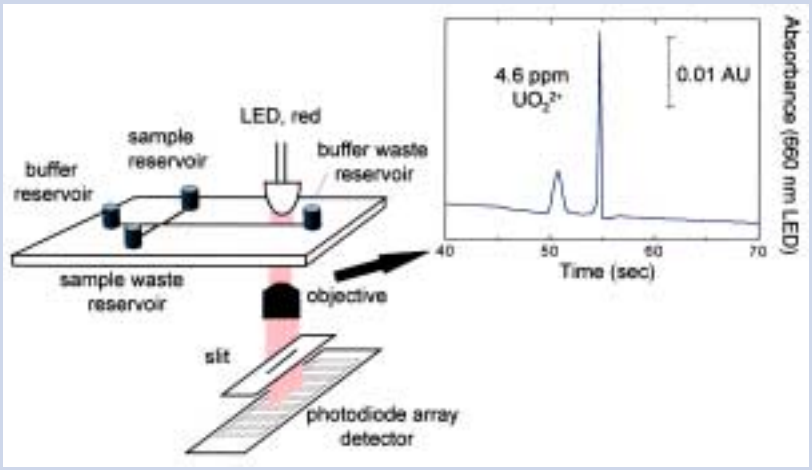
# DEACTIVATION AND DECOMMISSIONING (D&D)

## DECONTAMINATION COULD YIELD LARGE SAVINGS FOR LONG-TERM STORAGE AND RETURN VALUABLE MATERIALS FOR REUSE

The National Research Council's *Interim Report for the Committee on Long-Term Research Needs for D&D at DOE Sites (2000)* recommended basic research toward the development of real-time, minimally invasive, and field usable techniques to locate and quantify contaminants that are significant to D&D. Three EMSP analytical chemistry projects involve applications of such new techniques. One is exploring development of a portable radionuclide analyzer using capillary electrophoresis on a chip. Another is investigating a unique colorimetric sensing system based on polymerized crystalline colloidal arrays, and a third project is exploring the use of terahertz time-domain spectroscopy and imaging for identification of asbestos in real time. An engineering science project developed techniques necessary to produce gamma detectors for improved image resolution for depth profiling of surface radionuclide contamination.

More effective methods for decontamination of metal surfaces could yield enormous savings, not only because of the value of the reclaimed metals but also because of the reduced volume of materials put into a waste repository. EMSP projects include two studies involving the use of supercritical fluids for surface cleaning. Most radionuclides that are adsorbed onto metal surfaces are trapped in the surface oxide layers, so removal of the oxide layer would also remove the contaminants. Substances being investigated for surface oxide removal include naturally occurring organic chelates, biopolymers produced by algae, iron-reducing bacteria, and citric and related organic acids. A study of surfactants for removal of organic materials from metal surfaces led the investigators to find a simple modification that greatly improved surfactant performance.

A number of different surface heating methods have been proposed as alternatives to mechanical surface removal, so an EMSP project was designed to study the effect of heating on the engineering properties of concrete and on radionuclide removal.




**A Portable Sensor for Radionuclides and Heavy Metals**
A Naval Research Laboratory project (64982) is developing a sensitive, selective, portable sensor for radionuclides and heavy metals for use at DOE remediation sites so that lengthy analysis times at external laboratories can be avoided.

### PROBLEMS/SOLUTIONS

- Characterization is one of the most significant costs for D&D operations, and current methods for surface contaminants often require expensive laboratory determinations. Some state-of-the-art alternatives to traditional laboratory methods are being explored by several EMSP projects that were awarded in 1998.
- Gamma-ray spectroscopy and imaging with germanium detectors allow quick, accurate identification and spatial mapping of radioactive contaminants. However, current detectors have image resolution that is sometimes inadequate, so new techniques for producing detectors with improved resolution will form the basis for high-performance gamma-ray imaging systems.
- Past removal of organic materials from metal surfaces was usually done with chlorinated organic solvents that resulted in extensive subsurface pollution, so alternatives are needed for the removal of oil and other organics. While investigating use of conventional surfactants for removing oil from surfaces, some EMSP research workers found a way to make an order-of-magnitude improvement in the rate of oil removal.

### ANTICIPATED IMPACT

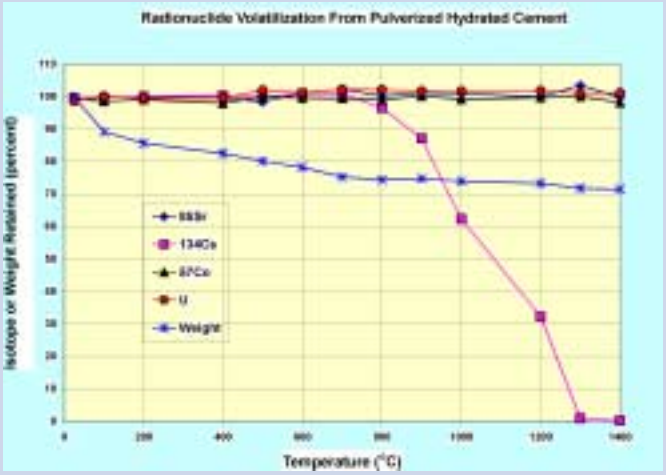
- There are 7,000 surplus buildings with a total area of contaminated concrete surfaces of about 18,000 acres in DOE facilities. The current method for removing surface contamination from concrete involves grit blasting, which removes large volumes of residue that contains small amounts of hazardous materials. Several EMSP projects are exploring new techniques for surface cleaning that would produce much less secondary waste at lower costs and with lower risks to workers.
- Reclamation of metals in DOE facilities would not only yield materials worth a billion dollars but would also save large costs for long-term storage of huge volumes of materials. Most of the radionuclide contaminants are contained in the oxide coating of the metals, so EMSP projects have investigated numerous potential technologies for surface oxide removal.

## Characterization of Contaminants

*A Portable Sensor for Radionuclides and Heavy Metals.* The goal of a Naval Research Laboratory/Geo-Centers project (64982) is to develop a sensitive, selective, portable sensor for radionuclides and heavy metals for use at DOE remediation sites so that lengthy analysis times at external laboratories can be avoided. The plan is to form metal complexes with highly selective complexing agents, and to separate them using capillary electrophoresis on a microchip with either absorbance or fluorescence detection. An example of a system for fluorescence detection was a rhodamine tagged calixarene, which has enormous selectivity for uranyl ions over other metals. The metal complex could be separated and detected on the microchip in less than 45 seconds. Absorbance detection was used with complexes formed by a commercial dye, Arsenazo III. By adjusting separation conditions, the dye could be used for a simple, highly selective and sensitive detection of uranium with a detection limit of 27 parts per billion (ppb). High-resolution separation and detection of seven common transition metals in the high ppb range was achieved with another commercial dye, and the analysis was done in less than a minute.

*Colloidal Arrays for Chemical Sensing.* A University of Pittsburgh project (65001) is exploring applications of a new type of chemical sensing system based on polymerized crystalline colloidal arrays, which were previously developed by the principal investigator. The sensor is based on a periodic array of colloidal particles that are polymerized into an acrylamide hydrogel. This periodic, colloidal array diffracts light in the visible spectral region. The particles also contain chelating agents to bind metal ions, and when a metal ion diffuses through the gel and binds to the colloid sites, the array is slightly distorted. The resulting change in diffraction wavelength can be used to determine the concentration of the target analyte. The plan is to develop simple, inexpensive new sensing materials that can be used as visual color test strips to report on the concentration and identity of such species as lead, uranium, plutonium, strontium, mercury, and other metal ions. Arrays of these sensing materials could also be attached to fiber optic bundles to simultaneously monitor numerous analytes.

*Terahertz Spectroscopy and Depth Profiling Using Gamma Spectroscopy.* Concrete and asbestos-containing materials that are contaminated with radionuclides are very difficult for D&D personnel, and alternatives to bore sampling could reduce costs and safety hazards to workers. A Rensselaer project (65004) has two objectives: (1) to develop methods for identification of asbestos in real-time in the field using terahertz (THz) time-domain spectroscopy and imaging, and (2) to develop methods for determining radioactive contamination depth profiles in the field using gamma spectroscopy. They have obtained measurements of the transmission of asbestos in the THz or far infrared spectral region, but spectral signatures in the initial region studied were insufficient for identification. The radiological contamination depth profiling studies are based on in-situ gamma spectroscopy, and the method requires data from a limited number of traditional bore samplings for calibration. The method has been shown to have very good predictions for the depth of point contaminants.




**Effect of Heating on the Properties of Concrete**
An ORNL/Northwestern University project (64896) has studied the effect of heating on the engineering properties of concrete as well as on removal of common radionuclide contaminants. The graph above shows retention of radionuclides and moisture by pulverized hardened cement paste when heated sequentially to increasing maximum temperatures.

*Germanium Gamma-Ray Detectors for Imaging Applications.* A critical component of the decontamination and decommissioning effort is the characterization of radioactively contaminated equipment and structures. The primary objective of an LBNL project (65015) is to develop the technologies necessary to produce large-area germanium (Ge) gamma-ray detectors with combined imaging and spectroscopy capabilities superior to that of presently available technologies. The LBNL group has further refined their existing Ge detector fabrication processes in order to produce the finely segmented, position-sensitive detectors needed for imaging applications. Several detectors have been produced, and a new technique for extracting the depth of gamma-ray interaction within the detector has been demonstrated. This technique will lead to improved image resolution. Furthermore, with these detectors, techniques have been devised to overcome energy resolution degradation effects that can occur in the detectors, thereby enhancing detection sensitivity and specificity. Their plan is to combine the newly developed detector technologies with unique electronics also being developed as part of the project in order to produce a prototype instrument for field testing.

## Decontamination of Metal Surfaces

*Micelles in Supercritical $CO_2$ for Actinide Extractions.* A LANL research program (64865) is investigating micelle formation in supercritical carbon dioxide ($scCO_2$) for use in extraction of actinides and other metals from surfaces. Fluorinated surfactants are used to form aqueous micelles, which can also be formed with acid solutions. The $scCO_2$ is able to penetrate pores in surfaces much better than pure water, and the tiny acidic water micelle droplets can still dissolve metals or metal salts. The metal can then be recovered simply by reducing the pressure, which causes phase separation with the metal in the aqueous phase. The ability of the microemulsion to concentrate the metal into a small volume of water makes it attractive for extractions from contaminated solids that have small amounts of metals or metal oxides dispersed over a large volume of solid waste, and the goal is to remove the contaminants into a much smaller volume than produced by other surface cleaning techniques.

*Actinide Complexing Agents in Supercritical $CO_2$.* An ANL/Loyola University/Notre Dame group (64965) is also exploring the use of $scCO_2$ as the solvent for removal of actinides from surfaces, but their work involves the synthesis of actinide complexing agents that are soluble in $scCO_2$. Diphosphonic acid ligands are known to form very stable complexes in actinide metal ions in both aqueous and organic solutions, but they tend not to be sufficiently soluble in $scCO_2$. So the group has prepared a number of alkyl- or silyl-containing derivatives, and in general they have similar abilities to form complexes with metals as do the parent diphosphonic acids. Unfortunately, the new derivatives still did not have sufficient solubility in supercritical carbon dioxide, so a number of new derivatives were being prepared in a search for more soluble ligands.

*Naturally Occurring Organic Agents for Surface Oxide Removal.* Steel and iron develop surface oxide layers where radionuclides and other contaminants are retained by a variety of mechanisms. There are huge inventories of contaminated metals throughout the DOE complex, so an efficient method for decontamination could yield large savings from reclaimed metals as well as avoidance of disposal as waste. The objective of a PNNL/LBNL/Ohio State project (64947) is to identify naturally occurring organic chelates (siderophores) that are effective at removing the surface oxides from metals so that the contaminants would also be removed. Dissolution studies with hydroxamic acid-type ligands have shown that dissolution rates of iron oxides increase by an order of magnitude as the number of functional groups per molecule increases. Modeling studies led to structure-activity relationships for catecholamide ligands and suggest that this method can be used to screen other similar ligands to select candidates for experimental study.

### Project Teams

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  PI: George Xu (65004)
- Lawrence Berkeley National Laboratory
  PI: Mark Amman (65015)

*Biopolymers for Surface Oxide Removal.* Polysaccharides that are generated by microorganisms form complexes with heavy metals, and they form viscous aqueous solutions that allow them to coat metal surfaces. An ORNL group (64907) cultivated several varieties of algae to produce biopolymers for removal of hazardous metals from surfaces. They have used both reconstituted biomass and partially purified polysaccharides for their studies, and screening studies using uranyl removal were used to select the most promising materials. They have studied uranium and other heavy metal removal from contaminated steel coupons using quantitative determinations of both surface and solution concentrations of the metals, and they have also tested the gel properties of the materials best suited for extended contact with surfaces so that the amount of worker time spent in decontamination activities will be minimized.

*Iron-Reducing Bacteria for Surface Oxide Removal.* Another approach to bioremediation of metal surfaces is being investigated by a PNNL/Montana State/University of New Hampshire group (64931). Their work is designed to determine if iron-reducing bacteria can quantitatively dissolve amorphous and crystalline iron oxides via anaerobic

respiration. The research is designed to determine the role of oxide structure and composition on bacterial attachment and subsequent reductive dissolution of iron oxide corrosion products from several varieties of steel. Another task is to identify how soluble electron shuttles can facilitate the rate and extent of microbial reduction process, particularly for surface features and pores inaccessible to bacteria. For example, they have shown that microbially reduced anthroquinone disulfonate can increase the rate and extent of iron oxide reduction as well as markedly increasing the solubility of plutonium by reduction of Pu(IV) to Pu(III). Another task is to investigate distribution of the radionuclides released during the dissolution of oxide films so that the actinides can be concentrated with a minimum of secondary waste generation.

*Naturally Occurring Organic Acids for Removal of Contaminants from Metal Surfaces.* A BNL/Stony Brook project (64946) was designed to address fundamental issues related to the removal of radionuclide contamination from metal surfaces using dilute solutions of citric and related acids. They have synthesized a number of uranium containing iron oxide phases commonly found on corroding metal surfaces and found that uranium was associated with the iron oxides as an inner sphere complex or as a uranyl-hydroxo complex. Dilute citric acid solutions were effective at removing uranium from corroded steel coupons that had been exposed to uranyl nitrate. Because it is important to avoid the generation of large volumes of secondary waste, another aspect of the work involved the recovery of radionuclides in a concentrated form by biochemical and photochemical degradation of the citric acid solutions.

*Surfactants for Removal of Organics from Metal Surfaces.* An ORNL/University of Tennessee team (64912) is conducting an investigation of surface decontamination with aqueous surfactant cleaners. Their work has focused on the need for removal of organics (oils, PCBs, etc.) from metal surfaces and other solid substrates. They have used several types of commercial surfactants to investigate the removal of oil from surfaces and have studied the factors that affect oil droplet detachment from metal surfaces. A simple modification that reduces detachment time by two orders of magnitude is being tested with a company that produces industrial cleaners. The goal of another part of the work is to design separation systems so that wastes are minimized and useful materials such as the surfactants may be reclaimed for reuse.

## Decontamination of Concrete Surfaces

*Effect of Heating on the Properties of Concrete.* An ORNL/Northwestern University project (64896) has studied the effect of heating on the engineering properties of concrete as well as on removal of some common radionuclide contaminants. Cured cement powder samples were spiked with short-lived isotopes cesium, strontium, and cobalt as well as uranium. Heating of these samples up to 1300°C resulted in complete vaporization of cesium, but negligible vaporization of the other radionuclides. The extraction of these radionuclides with water and dilute acids has also been measured before and after heat treatments. Work on the mechanics and thermodynamics of the process concentrated on computational simulation of concrete spallation induced by rapid heating, both by conductive heating from the surface and by microwave heating. The results suggest that conductive heating from the surface produces crumbling of the surface mainly by thermal stresses, but microwave heating produces pore pressures up to 100 atmospheres, which is sufficient to cause spalling.

## PCB Decontamination

*Extraction and Destruction of PCBs in Superfluids.* There are currently about 19,000 cubic meters of PCB-contaminated waste at DOE sites. Although there are several alternatives available for the destruction of these persistent pollutants, no method is clearly superior. A group project (64979) at the University of South Carolina, Clemson University, and the Savannah River Technology Center was begun to investigate a combined extraction and destruction process for decontamination of PCB-contaminated materials at DOE sites. The work involves studies of extraction with either supercritical $CO_2$ or hot water, followed by destruction of the extracted PCBs with either electrochemical or hydrothermal oxidation. The extraction of surrogates for PCBs from a commonly used adsorbent with supercritical $CO_2$ was promising, although not quantitative. A high-pressure reactor for conducting electrochemical superoxide chemistry in high-pressure $CO_2$ is being tested. A continuous-flow supercritical water oxidation apparatus has also been constructed and tested. The goal is to select the most successful elements of all the various processes that are being studied.

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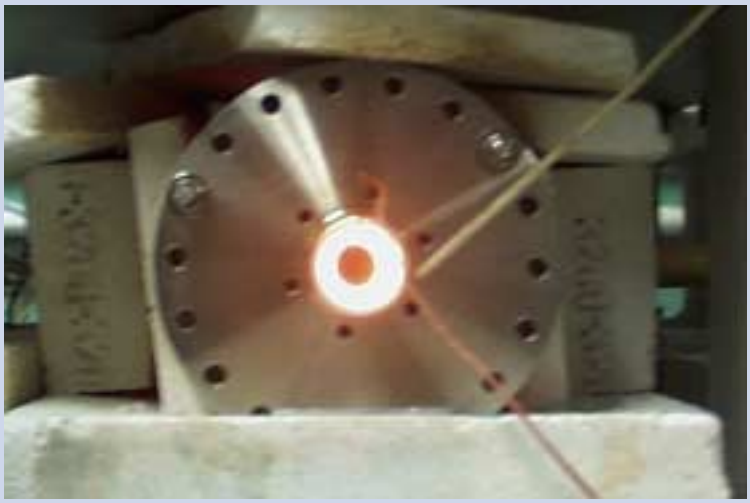
# HIGH-LEVEL WASTE – CHARACTERIZATION, SAFETY, AND IMMOBILIZATION

## RESEARCH IN THIS AREA HAS INVOLVED COLLABORATIONS BETWEEN SCIENTISTS AT MAJOR UNIVERSITIES AND NATIONAL LABORATORIES

The contents of the 282 major storage tanks at five major DOE sites are quite diverse, so characterization of materials in every tank is important not only for planning all treatment operations but also for safe storage practices. Some of the most exciting new analytical tools are being applied to problems in this area. A leading laboratory in the development of microcantilever sensors is working to develop microsensors that can be used for in-situ measurements of both chemical and physical properties. Another project is developing micromachined platforms for mounting up to 600 sensing elements in a small volume. Laser vaporization has many advantages for introducing high-level samples into a mass spectrometer, and another research effort has been directed toward basic understanding of the process in order to enable more quantitative measurements.

Two EMSP projects described here are related to safety issues. One is a study designed to improve the collection of particulates during operations with high-level wastes to avoid releases to the environment, and the other is a study of the mechanisms of reactions of organic materials in the tanks that can lead to the formation of flammable gases.

Immobilization of wastes in glass is expensive and should be done with the maximum waste loading consistent with long-term stability. An international group of researchers has conducted a thorough study of the formation of spinels in molten glass because that is the factor that limits waste loading in most cases. The goal of another project was to develop analytical tools necessary for an advanced process control system for glass melters. Alternative solidification schemes for sodium bearing waste are being improved by another university/laboratory collaboration. Calcined waste is mixed with metakaolinite and water/sodium hydroxide solution and cured to form dense ceramic-like materials having leachabilities comparable with high-level waste glass.



**In-Situ Determination of Molten Glass Properties**
A key aspect of an MIT/PNNL/SRTC project (65435) is in-situ determination of molten glass properties in the melter. Above: Tests of a millimeter-wave mullite waveguide at 1200°C.

### PROBLEMS/SOLUTIONS

- As described in a Tanks Focus Area Science Need (S-WT-06-01), “improved understanding of waste components with limited solubility in glass is needed to improve waste loading in high-level waste glasses.” The formation of spinels is often the factor that limits waste loading, so one EMSP research program has involved an extensive study of the mechanisms of spinel formation in order to understand how it can be minimized.
- Although laser-assisted vaporization of high-level waste samples has many advantages, another Science Need (AR-WT-11-01) noted that “the development of calibration standards, calibration procedures, and method validation…is required.” A project awarded in 1998 is one of several EMSP projects devoted to the basic science required to satisfy this requirement.
- There have been very few in-situ measurements of glass properties that could be used to control the production of glasses for immobilization of wastes. The objective of a collaborative effort between leading university and national lab researchers is to develop a control strategy for melters that includes determinations of the properties of molten glass.

### ANTICIPATED IMPACT

- EMSP research advances science to solve problems associated with storage tanks containing highly radioactive wastes. But an important secondary result in this area, as in the other application areas, is to maintain the scientific infrastructure necessary for long-term environmental management, and EMSP programs have involved some of the nation’s leading scientists and have resulted in numerous publications in major scientific journals.
- It appears possible that advances in developing arrays of microsensors, including microelectromechanical devices, will lead to analytical tools for headspaces that can be used for in-situ characterizations of complex solutions. The determination of the concentration of materials in high-level tanks by such methods could save millions of dollars in costs for each tank.

# Technical Summary and Progress

## Characterization of High-Level Wastes

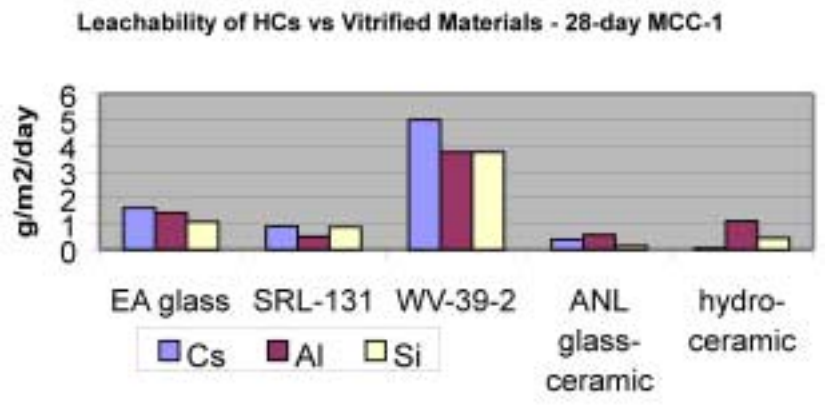
*Microcantilever Sensors.* Microcantilever-based sensors have been shown to be extremely sensitive devices that have been used to detect adsorption of molecules as well as changes in temperature, viscosity, or pressure. The goal of an ORNL/University of Tennessee project (65340) is to develop microsensors that can be used for in-situ chemical characterization as well as measurement of some physical parameters based on a combination of gravimetric and photothermal detection. They found that thiol-coated devices respond reversibly to the presence of certain phosponate molecules, and that they will also respond to the absorption of light by the adsorbed molecules. In order to increase selectivity, they have investigated applications of a number of chemically selective coatings, such as resins that have high specificity for cesium. Modifications to increase the surface area of the microcantilevers using sol-gels have also been explored, and studies of the responses of the devices to alpha and beta particles were also planned for future studies.

*Matrix Assisted Laser Desorption and Ionization.* The use of lasers to vaporize tiny amounts of material from a sample is particularly attractive for analyses of high-level wastes, and the technique has been widely used for introducing samples into a mass spectrometer. A Vanderbilt University/PNNL project (65425) began with studies of matrix-assisted laser desorption and ionization using a tunable, mid-infrared laser that can be tuned into vibrational bands of sodium nitrate. They have shown that they can detect molecular ions of major organic constituents of tank waste using the sodium nitrate as a matrix, and that adducts from the sodium nitrate can be used as an intrinsic internal standard. The maximum sensitivity demonstrated so far is in the few attomole range. Significant progress has been made in understanding the mechanism of charge generation and transfer during the desorption process so that the process can be certified.

*Temperature-Programmed Gas Microsensors.* A NIST/University of Maryland effort (65421) is directed toward the development of low-cost, reliable sensors for continuous monitoring of gas-phase species. Micromachined platforms called "micro-hotplates" have been replicated to produce arrays with up to 340 elements. The elements include functionality to rapidly measure and control temperature and to measure the electrical conductance of deposited oxide-based sensing films. As gases are adsorbed onto the oxide films, changes in their conductances will occur. Selectivity for analysis of gas mixtures is accomplished using oxides of varied composition and microstructure, as well as by varying the temperature at which each microsensing element is operated. Temperature programmed sensing utilizes transients in adsorbate coverages created as the temperature is varied rapidly to yield response signatures that can be analyzed by chemometric or neural-network methods. The temperature programs and sensing film materials within an array can be tuned for monitoring specific gases within different environments.

## Safe Waste Storage and Interim Storage

*Improved Collection of Aerosols.* Aerosols that are formed during calcining, for example, are difficult to contain and present a potential for release of radioactive materials. Because the collection efficiency for most particulate collection technologies increases as the particle size increases, methods for increasing the size of particles in an effluent stream should optimize aerosol capture processes. This is the basis of an ORNL/University of Texas project (65328) that is conducting both theoretical and experimental studies of electrical and acoustic methods to cause aerosol particles to coalesce to form larger particles. Experimental conditions involving spherical particles falling through a vibrating glycerin bath have been designed to match closely those of acoustic agglomeration of aerosols, and another apparatus has been built to study the agglomeration of aerosols in flowing gas streams with applied acoustic and/or electric fields. Attempts have been made to use experimental conditions that match the aerosol characteristics of potential applications so that the results may lead to practical implementation.




**Inexpensive Zeolite Containing Waste Forms**
Zeolites are often used in the nuclear industry for absorption and immobilization of radionuclides. A new process has been developed in which a hard, ceramic-like material containing zeolites is prepared from metakaolinite mixed with calcined sodium-bearing tank waste. A Penn State University project (65366) has examined the usefulness of these materials for immobilizing low-level radioactive waste.

*Formation of Flammable Gases in Tank Wastes.* The organic compounds that are included in some high-level waste tanks degrade to flammable gases, such as hydrogen, ammonia, and organic vapors. The reducing characteristics of organic

chemicals also cause interferences with removal of radionuclides during pretreatment operations. To understand potential hazards and interferences with tank remediation processes, it is necessary to know the reactions that have occurred as a result of extended exposures to high radiation levels and to elevated temperatures. Several other EMSP projects have studied radiolysis of these organic materials, so the objective of a PNNL project (65408) is to investigate reactions that can occur in the absence of radiation. Of the major complexing agents used at Hanford, only HEDTA and glycolate are readily oxidized by thermal reactions to give flammable gases. The oxidizing agents for these reactions are nitrites and aluminate ions or other aluminum species are the catalysis, but this work has shown that previously accepted mechanisms for the reactions were not correct. New mechanisms for oxidation of glycolate, HEDTA, and related structures are being explored.

### Waste Immobilization

*Formation and Behavior of Spinels in Glass*. The fraction of high-level waste that can be incorporated in glass is limited by the formation and settling of crystalline spinels because they interfere with melter operation. The objective of the PNNL/Czech Academy/Glass Service project (65422) is to gain a fundamental understanding of the formation and behavior of spinels in glass in order to learn how to increase waste loadings by several mass percent. They have developed a mathematical model describing the electric, temperature, and velocity fields in a melter, a model of spinel settling in glass melt, and a physical model to verify the results of the mathematical models. They have found that spinel crystals form during the initial melting stages, dissolve during the final stages of glass formation, and then form again when the temperature drops below the liquidus temperature. In addition to the major spinel-forming nickel, chromium, iron, and manganese oxides, the concentration of some minor components, such as ruthenium and silver oxides, can affect the number, density, and size of spinel crystals.

## Project Teams

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*Inexpensive Zeolite Containing Waste Forms.* Zeolites are often used in the nuclear industry for absorption and immobilization of various radionuclides. A new process has been developed in which a hard, ceramic-like material containing zeolites is prepared from metakaolinite mixed with calcined sodium-bearing tank waste. A Penn State University/SRTC project (65366) has examined the usefulness of these materials for immobilizing low-level radioactive waste. Experiments have been performed in order to determine the conditions needed to maximize the zeolitization process. Various proportions of metakaolinite, calcined waste, and water were cured as a function of time and temperature. Very encouraging results have been obtained in leach tests with these hydroceramics—sometimes exceeding the leach-safe characteristics of high-level waste glass. Hydroceramics appear to offer a viable alternative to vitrification at substantial savings in cost.

*In-Situ Determination of Molten Glass Properties.* Active feedback control of glass melters would maximize waste loading and would insure that a high-quality glass product is reliably produced. Consequently, significant cost savings would be realized for high-level waste immobilization by a more efficient vitrification process and minimized glass product volume. Project 65435 is a three way collaboration between MIT\PNNL\SRTC to develop new advanced melter sensors, obtain new glass melt data, and develop an advanced melter control strategy using the new sensor technologies and new glass data. In-situ determination of molten glass properties in the melter is a key aspect of this work. Robust new sensor technologies using millimeter-wave electromagnetic radiation for the determination of temperature, emissivity, viscosity, and density and are being developed and tested. Glass measurements are being obtained that correlate the measurable physical properties with the chemical composition. The goal is to develop an advanced process control system that uses direct measurements of glass properties as an integral part of the melter control system.


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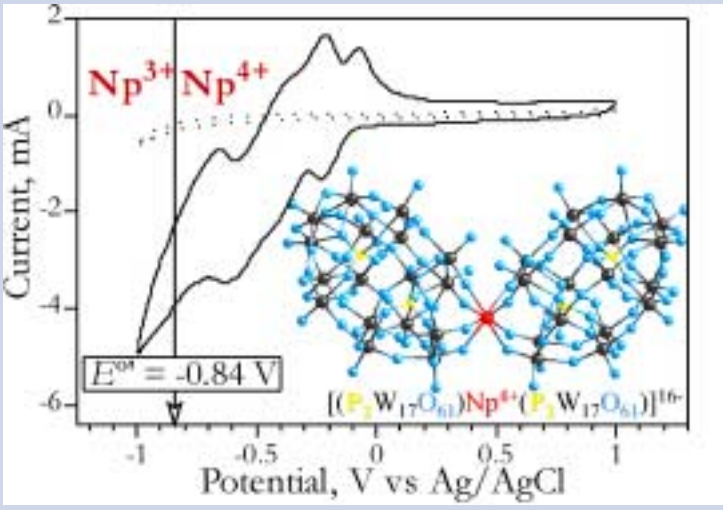
# HIGH-LEVEL WASTE – RETRIEVAL AND PRETREATMENT

## More reliable and efficient methods for waste retrieval and radionuclide removal could yield large savings in life-cycle costs

EMSP projects related to the retrieval of tank wastes include a numerical modeling study of the complex interactions of chemical reactions, waste flow properties, and slurry mixing. Another program found that boehmite is always the most stable form in highly alkaline conditions, and the focus of one effort was on the recovery and reuse of sodium hydroxide from alkaline tank wastes. Finally, leaks have already occurred from Hanford tanks and additional losses may occur during retrieval operations, so another project focused on the migration patterns of this highly radioactive waste in the vadose zone beneath the tanks.

Pretreatment is designed to remove radionuclides for high-level storage so that the majority of the tank contents can be stored as low-level wastes. One project investigated details of aluminum chemistry needed to optimize its removal from sludges, while another determined the solubility of chromium compounds. The removal of aluminum and chromium compounds is necessary to minimize the volume of high-level waste for immobilization, but it is also important that the actinides not be removed during these procedures. A thermodynamic database for actinides in highly alkaline conditions was the subject of an investigation, while another determined leaching of actinides from sludges that simulated those formed from three different processes at Hanford. Two studies explored methods for removal of actinides from solution. One of these investigated the usefulness of transition metal oxide clusters to sequester actinides for subsequent vitrification, and another prepared high-capacity sorbent materials for selective actinide removal. Exploratory studies of new methods for cesium and pertechnetate removal were the subjects of two other efforts.




**Leaching of Actinides from Tank Sludges**
The work of an Argonne National Laboratory project (65378) emphasized the leaching of actinides from materials that simulated the sludges formed from several different plutonium purification processes at Hanford and the speciation of actinides in concentrated alkali. Above: Cyclic voltammogram of the neptunium "butterfly" complex, $[Np(P_2W_{17}O_{61})_2]^{16-}$, with the Wells-Dawson polyoxoanion, $[P_2W_{17}O_{61}]^{10-}$ (P = yellow; W = black; O = aqua; Np = red). Actinide redox chemistry, like the one-electron $Np^{4+}/Np^{3+}$ couple, is a strategic issue concerning the prospective use of electroactive polyoxometalate clusters as inorganic complexants of actinides in radioactive waste processing.

### Problems/Solutions

- As described in an STCG need related to treatment of high-level wastes (RL-WT041-S), "a lack of fundamental knowledge about the distribution of radionuclides in the high-level waste stream significantly impacts the number of glass logs requiring disposal and as a result the ultimate high-level waste disposal cost." Several research efforts were directed toward unraveling the speciation of actinides in highly alkaline environments.
- Systematic studies of the parameters that affect the rates of dissolution and solid-state transformations of aluminum-containing phases are presently unavailable despite the fact that they are the most prevalent solids that can appear or disappear during high-level waste processing. An EMSP project was designed to rectify this deficiency and has found that boehmite is always the most stable aluminum-containing solid in highly alkaline wastes.
- If sludge-washing operations to remove aluminum and chromium, for example, result in dissolving some of the actinides, the latter must be removed. Two major projects were focused on methods for selective removal of actinides from these solutions.

### Anticipated Impact

- The *Status Report on Paths to Closure* (March 2000) estimated that the life-cycle cost for high-level waste remediation through 2070 will be as much as $58 billion. Because most of the tank remediation efforts will occur after 2006, basic research efforts could still lead to new technologies that could produce large savings over the projected costs.
- As outlined in STCG Need RL-WT023, information is needed to predict solids precipitation, gel formation, and the structure of solids that form in retrieval, wash, and leach solutions so that precipitations and gel formation can be avoided. Several EMSP projects are directly investigating basic issues related to these concerns, and their work should contribute to the avoidance of large expenses that will be incurred if transfer lines become plugged during waste retrieval.

# Technical Summary and Progress

## Waste Mobilization and Retrieval

*Numerical Modeling of Slurry Mixing.* All high-level waste treatment operations are dependent upon removing the waste from a tank by installing mixer pumps that stir up the sludge, saltcake, and supernatant liquid to form a slurry that can be pumped out of the tank. The objectives of a University of Minnesota/PNNL project (65371) are to study the complex interactions of chemical reactions, waste rheology, and slurry mixing. Their numerical modeling work includes evaluations of chemically active, non-Newtonian tank waste mixing, coupled with chemical reactions and realistic flow parameters. They have confirmed the importance of accounting for yield strength in non-Newtonian sludge mobilization, and their modeling studies are being used in tank waste mixing test plans at Hanford. Another study indicated that dissolution of sodium nitrate and sodium nitrite during mixing changed the waste's physical properties and flow characteristics, further affecting waste mixing. Other areas include studies of local areas of unwanted chemical reactions and conditions that might lead to the formation of gels that are almost impossible to pump. These findings will assist in development of optimal procedures for safe, effective waste retrieval.

*Aluminum Compounds in Tank Wastes.* Aluminum-containing phases are the most prevalent solids that can appear or disappear during high-level waste processing, and the unexpected formation of precipitates could be a serious problem during retrieval activities. The goals of a PNNL/Princeton/SRTC project (65411) were to identify aluminum-containing phases and to predict the conditions under which they can form. The two most widely observed phases of aluminum in alkaline wastes are gibbsite and boehmite, and the latter is the slow dissolution phase and is of greater concern. The work in this project has concluded that in alkaline solutions boehmite is always the stable phase, and that gibbsite tends to transform to boehmite. The mechanism of the transformation can vary with different circumstances, but the existence of high concentrations of nitrate salts, for example, delayed but did not stop the transformation to boehmite. Therefore, the behavior of the boehmite phases must be understood to predict the efficiency of tank waste processing.

*Separation and Reuse of Sodium Hydroxide in Waste Tanks.* Most high-level waste tanks contain high concentrations of sodium hydroxide and other sodium salts. The major objective of an ORNL/University of North Texas project (65339) is to extract selectively sodium hydroxide from high-level waste in Hanford and Savannah River tanks so that it may be used in waste retrieval and sludge washing operations. A method being tried is to use a weakly acidic alcohol, such as a highly fluorinated long-chain alcohol, that is soluble in an organic solvent that has very little solubility in water. When the alcohol is exposed to a highly alkaline water solution, it is converted to the sodium salt but remains dissolved in the organic solvent. When the latter solution is stripped with water, the alcohol is regenerated, leaving sodium hydroxide in the water. Synergistic effects in sodium hydroxide separations have been found when extractants, such as crown ethers, are combined with the fluorinated alcohol. Experiments are being conducted to increase the extraction efficiency enough to enable 90% of the sodium hydroxide to be removed from the tank waste.

*Migration of Waste Leaked from Hanford Tanks.* As much as a million gallons of concentrated solutions may have leaked from Hanford tanks and additional liquid may be added to the tanks during retrieval operations, so understanding the migration of this highly radioactive and hazardous waste in the vadose zone beneath the tanks is the goal of a PNNL/DRI/Oregon State University project (65410). Using X-ray tomography for laboratory studies of the migration of concentrated sodium nitrate solutions through Hanford sediments, they have shown that the high surface tension of a salt solution has a higher migration velocity because of decreased wettability. In addition, as a result of the osmotic gradient, water from surrounding areas migrates into the plume and causes more rapid downward migration. Ongoing field studies are underway to study migration patterns in two types of Hanford sediments. As the salt concentration increases, the surface tension of a solution increases and wettability decreases, so the modeling studies have focused on the consequences of these phenomena, particularly in causing more rapid migration toward groundwater in small columns or fingers.

## Waste Pretreatment

*Removal of Aluminum from Tank Sludges.* Washing the sludge in high-level waste tanks with concentrated sodium hydroxide solutions has been proposed as a method to remove aluminum (as the aluminate ion) in order to enable a reduction of the amount of high-level waste that must be immobilized. However, if the solubility of uranium and other actinides in the sludge is also enhanced by sludge washing, then the purpose of the washing may be partially defeated. A LANL/Russian Institute of Physical Chemistry project (65318) was designed to study the chemistry of actinides under highly alkaline conditions, particularly on the interaction of actinides with aluminate ions under highly alkaline conditions. The solubility of actinyl increases with increasing aluminate concentrations, but the cause was found to be indirect rather than by formation of an aluminate-actinyl complex. They have also found changes in aluminum chemistry when uranium is present, including precipitation reactions that do not occur in the absence of the uranyl species. Similar studies are underway to investigate plutonium chemistry under highly alkaline conditions, and results of this study will assist the development of pretreatment operations.

*Removal of Chromium from Tank Sludges.* The presence of chromium (Cr) compounds in tank sludges greatly complicates the vitrification process because the Cr compounds tend to form separate phases in molten glass. Current sludge washing processes are not effective in removing sufficient Cr without excess solubilization of actinides and other radionuclides. So a PNNL/LBNL/Washington State University project (65368) was designed to measure the solubility of various Cr compounds as well as rate constants for oxidizing Cr(III) compounds to the more soluble Cr(VI) species. They have found that the solubility of amorphous chromium hydroxide increased dramatically with increasing alkalinity of the solvent, and it also increased with increasing sodium nitrate concentrations in the solutions. The rates of oxidation of various Cr(III) species were also studied, and hydrogen peroxide was found to be an effective oxidant for solubilization of chromium hydroxide but not for crystalline chromium oxide.

*Thermodynamic Data for Actinides in Alkaline Systems.* Actinide speciation in high-level wastes is the subject of a Washington State University/LBNL/University of Idaho project (65352), which is focused on developing a thermodynamic database of plutonium and other actinide complexing in alkaline systems with elevated temperatures and electrolyte concentrations. Stability constants and thermodynamic quantities are being measured under alkaline conditions for both chemical analogs of plutonium and plutonium itself. Their goal is to add the actinide information to the temperature dependence thermodynamic models so that reliable predictions can be made for the speciation of actinides over all ranges of temperatures and ionic strengths relevant to treatment and disposal of high-level wastes.

*Leaching of Actinides from Tank Sludges.* Another study of actinides in tank wastes was pursued by an ANL/LBNL project (65398). This work emphasized the leaching of actinides from materials that simulated the sludges formed from several different plutonium purification processes at Hanford and the speciation of actinides in concentrated alkali. The sludges were spiked with tracer concentrations of uranium, neptunium, plutonium, and americium and then subjected to alkaline and exploratory acidic scrubs. Both uranium and neptunium exhibited moderate solubility while americium and plutonium were less soluble, but there was some indication of colloidal transport of plutonium. Actinide solubilization often accompanies dissolution of iron, chromium, and manganese oxides from the sludges. Electrochemical, spectrophotometric, and X-ray techniques have been used to explore the nature of actinide species in highly basic solutions, and they have found, for example, that $NpO_2(OH)_4^{3-}$, $NpO_2(OH)_4^{2-}$, and $NpO_4(OH)_2^{3-}$ are the dominant species of neptunium V, VI, and VII in strong base. Additional studies with water-soluble complexing agents were also being done.

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*Metal Oxide Clusters for Removing Actinides.* Polyoxoanions (POAs) are transition metal oxide clusters held together by metal-oxygen bonds. Examples include $[P_5W_{30}O_{110}]^{15-}$, $[Nb_6O_{19}]^{8-}$, and many others. Despite the complexity of these structures, many of them can be prepared simply and inexpensively and some are currently used in commercial catalytic processes. An ANL/Hunter College project (65378) was designed to investigate the formation of actinide-POA complexes that could selectively remove actinide ions from solution and then to determine whether these complexes could be used directly with glass vitrification to immobilize actinides. They have prepared a variety of lanthanide and actinide complexes and performed detailed structural studies of several of the lanthanide-POA complexes in order to better understand the binding mechanisms. A niobium species, $[Nb_6O_{19}]^{8-}$, has been studied because it is stable in highly alkaline solutions. They have examined the solubility of POAs in glass, and initial experiments with lanthanide-containing species suggested that the POA complexes decompose during vitrification with borosilicate glasses. Nonetheless, the decomposition produces a homogeneous mixture in glass, so the POA complexes may provide a useful form for actinide extraction and immobilization.

*High-Capacity Materials for Removing Actinides from Solution.* Low concentrations of actinides in the complex aqueous solutions in high-level tank waste or in the solutions from sludge washing most likely cannot be avoided, so the objective of a PNNL/ANL/LBNL project (65370) is to prepare high-efficiency, high-capacity sorbent materials for selectively removing actinides from these solutions. They have used supercritical carbon dioxide or nitrogen as the reaction medium for the deposition of self-assembled silane monolayers in mesoporous ceramic materials with the highest population density ever reported for such systems, and this procedure can be extended with a virtually limitless number of different ligands. Preliminary screening studies of these materials with lanthanides showed very high affinities for the metal ions with reaction times of less than a minute. Systems with high affinities for plutonium have been found, and one system has a high affinity for plutonium but almost none for americium at lower pHs, so this system may provide a simple method for separation of these two actinides in solution. Materials for the separation of all of the actinides from thorium through americium were being explored, and systems with cationic ligands on the mesoporous support were being investigated as agents for removing pertechnetate from solution.

*Separation of Cesium from High-Level Wastes.* The separation of cesium from high-level wastes can be achieved using certain crown ethers as complexing agents, but this procedure requires the use of undesirable organic solvents. A University of Idaho/PNNL study (65351) was designed to explore a variety of alternate conditions for extraction of cesium using crown ethers in solvents ranging from water to supercritical fluids. Nuclear magnetic resonance techniques were being used to study the cesium species present when water, chloroform, and crown ethers were present, and methods were also available for similar studies in supercritical carbon dioxide, $scCO_2$. Unfortunately, the cesium salts being studied were not soluble in $scCO_2$, so alternate anions were being synthesized to attempt to increase the solubility.

*Electroactive Ion-Exchange for Pertechnetate Removal.* The removal of pertechnetate anions from high-level wastes is important because technetium has a long half-life and pertechnetates are highly soluble and therefore mobile in the environment. With currently available ion exchange resins for pertechnetate removal, unwanted secondary wastes are generated either because of low capacities or because large volumes of hazardous eluents are required to regenerate the resins. A PNNL/BNL/University of Minnesota project (65409) has investigated electroactive ion exchange materials as an alternative for pertechnetate removal. These materials use electrically induced charges to expel the sorbed ions rather than requiring chemical eluents to exchange them. They have investigated ferrocene-containing polymers and have synthesized materials with higher alkaline stability than commercially available products. These materials still did not have adequate stability, so a variety of other polymers were being synthesized and characterized.

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# MAKING A DIFFERENCE IN THE VADOSE ZONE!

## EMSP Research Projects Focus on Solving Some of the Nation's Most Complex Environmental Remediation Challenges

**Exploring the Vadose Zone**
The Vadose Zone is the protective layer of soil and rocks between the dusty surface of the earth and the groundwater below. Vadose Zone research seeks better ways to monitor and remediate this region.

The Vadose Zone is the unsaturated subsurface between land surface and the top of a groundwater aquifer. This is one of the primary areas where contamination from leaks and spills can accumulate. The DOE has targeted this area as an opportunity where subsurface cleanup can occur before contamination reaches the groundwater. Targeted research in the Vadose Zone can make a significant difference in cleanup time and costs and reduce the risk to human health and the environment.

Mandated by Congress in 1996, the Environmental Management Science Program (EMSP) is a partnership between the Department of Energy (DOE) Office of Basic and Applied Research and the Office of Science. The purpose of the EMSP is to foster basic research that will contribute to successful completion of DOE's mission to cleanup the environmental contamination across the DOE complex.

## Integrating Research into Site Operations: Selected Highlights

***Characterization*** *– Developing better ways to locate and characterize subsurface contamination reduces uncertainty.*

**Project 70050 –** This project is developing a sensor technology to detect organic contaminants, such as solvents, in-situ at depth using a cone penetrometer. Such technology eliminates the need for expensive drilling and reduces the costs and risk associated with managing the drill cuttings as hazardous waste.

**Project 70052 –** This project is developing a technology that uses ground penetrating radar to locate chlorinated solvents in the subsurface. The principle investigator is currently working with personnel at Hanford and Savannah River to perform controlled experiments.

**Project 70010 –** Offering unprecedented levels of specificity, a sensor is being developed to monitor the vadose zone and groundwater for contaminants associated with high-level waste stored at Hanford. A similar sensor has already been successfully demonstrated at Hanford.

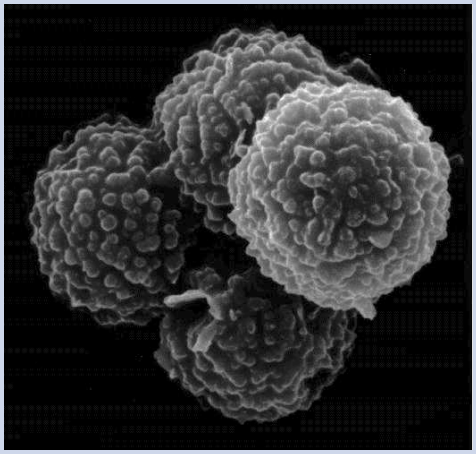
### Why Research?

- **The DOE Office of Environmental Management manages the most technically challenging and complex work of any environmental program in the world.**
- **Estimates for cleanup range from 151 to 195 billion dollars through the year 2070.**
  - Status Report on Paths to Closure, March 2000
- **"Scientific understanding of the factors that govern the long-term behavior of residual contaminants in the environment is not adequate."**
  - National Research Council Committee on Remediation of Buried and Tank Wastes
- **"A basic research program focused on EM's most difficult cleanup problems may have a significant, long-term impact on the EM mission."**
  - National Academy of Sciences

**Data Collection, Savannah River Site, SC**
Multi-offset, ground-penetrating radar data acquisition for DNAPL detection at the SRS (70052).

**Research Benefits:**

- Research targets soils at DOE sites such as Hanford and Savannah River
- Lower cost in-situ analysis techniques
- Non-penetrating characterization of contaminant plumes
- Enhanced decision making capabilities for estimations of waste volumes
- Lower volumes of secondary waste generated during site characterization.



**Colloid Formation, Hanford Reservation, WA**
Colloids, micron sized particles that behave as fluids and play a role in contaminant transport, formed during reaction of Hanford Sediments with simulated tank solutions (70135).

## *CONCEPTUAL/PREDICTIVE MODELING – MORE EFFECTIVE PREDICTIVE CAPABILITIES ENHANCE CLEANUP DECISION MAKING*

**Project 70135 –** This project is clarifying some of the complex reactions between colloids and contaminants and how this may impact contaminant migration at many of the DOE sites, including Idaho and Hanford.

**Project 70163 –** This project is solving the thermodynamic problems and reactions between Hanford tank wastes and subsurface sediments to support better decisions for remedy selection by cleanup project managers.

**Project 70219 –** This project is clarifying understanding of the complex processes that affect the fate and transport of radionuclides beneath the Hanford tank farms by experimenting with Hanford sediments and how they interact with tank wastes.

**Research Benefits:**

- Improved understanding and predictive capability of mechanisms responsible for the accelerated migration of radionuclides
- Strengthened knowledge base to better understand and predict the processes impacting contaminant migration
- More accurate estimations of the risks to human health and the environment from contaminants
- More accurate predictive information to support cleanup decisions
- Enhanced capabilities to support assessment of long term performance of remedial designs.


**Excavation of Radionuclides, Hanford Reservation, WA**
Fate and Transport of Radionuclides Beneath the Hanford Tank Farms: Unraveling Coupled Geochemical and Hydrological Processes in the Vadose Zone (70219).

## *CONTAINMENT AND STABILIZATION – CONTAINING AND STABILIZING SUBSURFACE CONTAMINATION OR INNOVATIVE REMOVAL REDUCES RISK TO HUMAN HEALTH AND THE ENVIRONMENT*

**Project 70035 –** This project seeks to better understand how the interactions between organic contamination and surface-active minerals and/or microorganisms effect the ability to contain and stabilize or remove contamination. This principle investigator is working with Savannah River personnel targeting specific problem areas and contaminants at the site.

**Project 70045 –** Chlorinated solvents are a problem at over 60% of DOE facilities. Better understanding the microscopic physical processes that may limit solvent recovery in the subsurface will enhance future remediation activities.

**Project 70054 –** This research is focused on altering the genetic properties of tobacco plants to remove mercury and other contaminants from subsurface soils at sites, such as Oak Ridge, where an effort is planned to field test this research.

**Project 70063 –** This project seeks to better define the processes and conditions that enhance the effectiveness of naturally occurring microorganisms to degrade solvents in the subsurface.

**Project 70088 –** Gas phase treatment with dilute hydrogen sulfide is a promising new treatment option to immobilize metals and radionuclides in the subsurface. Better understanding the primary reaction mechanisms has resulted in a successful field demonstration at the White Sands Missile Base.

**Research Benefits:**

- Influencing natural factors in the environment to enhance contaminant stabilization or removal
- Enhancing cleanup through understanding what factors limit these processes
- Manipulating genetic properties of plants to remove contamination from the subsurface
- Better understanding the conditions where natural degradation of contaminants is possible or may be enhanced
- Understanding the reaction mechanisms that impact new innovative treatment for contaminant immobilization.

## *Monitoring and Validation – Ensuring that cleanup decisions remain protective for the future*

**Project 70012 –** The use of microorganisms to clean up waste in situ is occurring at many DOE sites. This innovative technique will provide an effective, low-cost alternative to monitor the progress of these actions and ensure that decisions remain protective.

**Project 70115 –** This project is using radar technology to develop a method for non-invasive determination of moisture content. Moisture content is a critical parameter and early indicator of the potential for contaminant migration. This technique may reduce costs for long-term monitoring of containment units.

**Project 70179 –** Enhancing the ability to monitor radionuclides at extremely low levels, this project is targeting contaminants common in tank wastes at Hanford, Savannah River, and Idaho. Being able to monitor low levels in-situ enhances real-time decision making and eliminates the need for costly sampling and laboratory analyses.

**Research Benefits:**

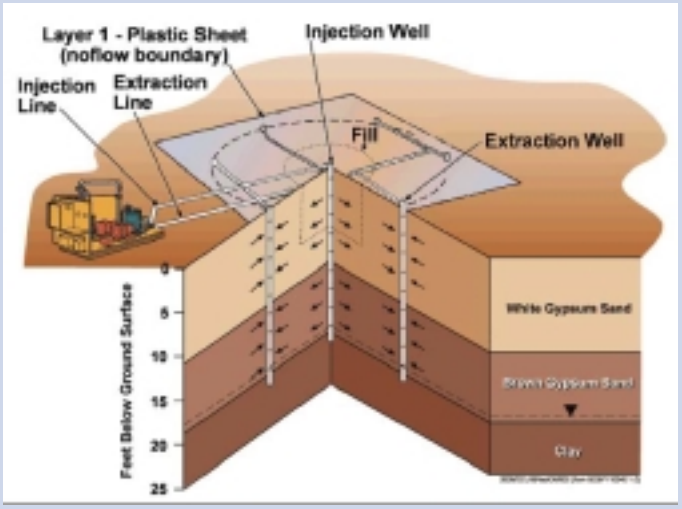
- Developing non-invasive technologies for monitoring the effectiveness of clean up remedies
- Reducing risks and costs associated with long term monitoring
- Enhancing capabilities for real time decision making.

### EMSP Objectives ...

- **Provide scientific knowledge that will revolutionize technologies and cleanup approaches to significantly reduce future costs, schedules, and risks**
- **"Bridge the gap" between broad fundamental research that has wide-ranging applicability, such as that performed in DOE's Office of Science, and needs-driven applied technology development that is conducted in EM's Office of Science and Technology**
- **Focus the nation's science infrastructure on critical DOE environmental management problems.**

### National Academy of Sciences– Research Needs in Subsurface Science, 2000 ...

- **"The committee identified significant knowledge gaps in the following process steps . . .**
  - **Location and characterization of subsurface contaminants and characterization of the subsurface**
  - **Conceptual modeling**
  - **Containment and stabilization**
  - **Monitoring and validation."**




**Field Demonstration, White Sands Missile Range, NM**
70%of Cr(VI) in the vadose zone has been immobilized. Excess $H_2S$ gas is largely consumed by interaction with soil, with no releases to the environment (70088).

EMSP
Environmental Management Science Program

Office of Science & Technology
Office of Environmental Management
U.S. Department of Energy

# UPCOMING RESEARCH

## FY2001 Research Awards Will Target Two Vital EM Problem Areas: Deactivation and Decommissioning and High-Level Waste

### *Deactivation and Decommissioning*

Basic research is being solicited under SC/EM Notice 01-19 in all areas of science with the potential for addressing problems in deactivation and decommissioning. Proposed basic research should provide SC and EM with near-term fundamental data that may be critical to the advancement of technologies that are currently under development, particularly regarding the following needs:

- Real-time characterization methods to support decision making
- Innovative decontamination approaches to reduce costs
- Remote systems to reduce worker exposure and risk.

### *High-Level Waste*

Basic research is being solicited under SC/EM Notice 01-16 in all areas of science with the potential for addressing problems in the cleanup of high level radioactive waste. Proposed basic research should provide SC and EM with near-term fundamental data that many be critical to the advancement of technologies that are currently under development, particularly regarding the following needs:

- Tank Closure
- Separation technology to reduce waste volume
- Waste immobilization research to reduce risk
- Real-time waste characterization to support all phases of cleanup.

**For additional information about the Environmental Management Science Program:**

- Visit our website at **http://emsp.em.doe.gov**, or
- Contact one of the following EMSP representatives:

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roland.hirsch@science.doe.gov
www.science.doe.gov

# EMSP COLLABORATIONS

Research results are not always directly transferred to a specific end-user. Collaborations or interactions between EMSP researchers and others occur that increase the body of knowledge in a specific area as a direct result of EMSP funded research. This comes in many forms:

42 Consulting - provide advice or technical expertise
46 Joint interaction - researcher and end-user in joint interaction
18 Mission directed - project direction provided by end-user
53 Program interaction - researcher to researcher interaction

This section describes the reported collaborations that have occurred within the EMSP. Numerous other less formal collaborations occur during the EMSP topical and national workshops. Many of these are anticipated to mature into the research partnerships and research transfers reported elsewhere in this document.

## DEACTIVATION AND DECOMMISSIONING

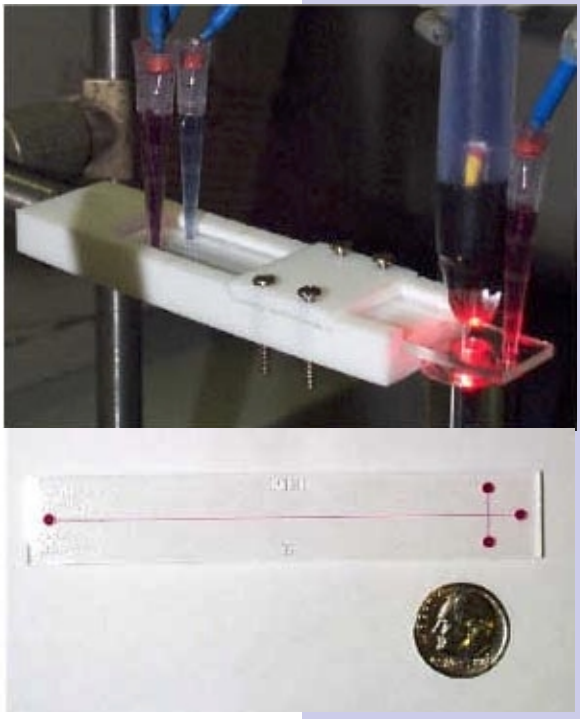
### Analytical Chemistry & Instrumentation

#### Project: 64982

*Title:* Metal Ion Analysis Using Near-Infrared Dyes and the "Laboratory-on-a-Chip"
*PI:* Dr. Greg E. Collins
*Institution:* Naval Research Laboratory

*Description:* This project addresses the need for developing a new class of radionuclide and heavy metal complexation agents that are tagged with near-infrared dyes and can therefore be extended to the implementation of a compact and portable "laboratory-on-a-chip" operable in the stringent field requirements of DOE site characterization and remediation. As such, this project is also working directly with the Nevada Field Office to address their need for uranium detection in soils and groundwater.
*Collaboration Type:* Joint interaction
*Fiscal Year:* 2001
*Collaborator:* John Jones and Bruce Crow
*Collaborating Organization:* DOE-NV

*Description:* This project addresses the need for developing a highly sensitive and selective portable radionuclide analyzer which would permit a low-cost and timely characterization of DOE remediation sites. Through the application of near-infrared



The portable Lab-on-a-Chip Sensor for Radionuclide and Heavy Metals is intended to provide a field portable characterization instrument for in-situ waste characterization. [see Project #64982]

fluorophore tagged macrocycles, in combination with the capillary electrophoretic separation of radionuclide and heavy metal complexes on a microchip, we propose an innovative, low cost characterization approach to gaining timely characterization data in the field. DDFA has committed to perform Large Scale Demonstration on the "Laboratory-on-a-Chip."

*Collaboration Type:* Joint interaction *Fiscal Year:* 1999
*Collaborator:* Dick Meservey
*Collaborating Organization:* INEEL

### Project: 65001

*Title:* Development of Novel, Simple Multianalyte Sensors for Remote Environmental Analysis
*PI:* Dr. Sanford A. Asher *Institution:* University of Pittsburgh

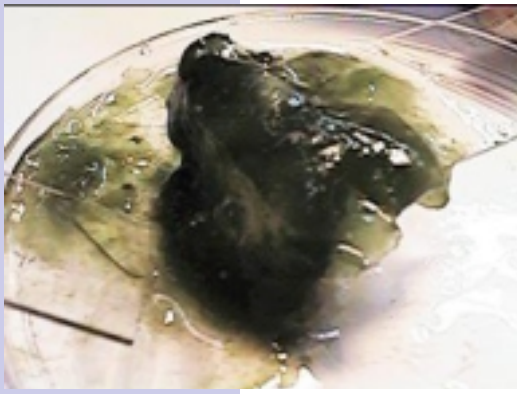
*Description:* When an analyte binds, its charge is immobilized within the acrylamide hydrogel. The resulting Donnan potential causes an osmotic diffracted wavelength shift and the color changes. The change in the wavelength diffracted reports on the identity and concentration of the target analyte. Our successful development of these simple, inexpensive highly-sensitive chemical sensing optrodes, which are easily coupled to simple optical instrumentation, could revolutionize environmental monitoring. In addition, we will develop highly rugged versions, which can be attached to core penetrometers and used to determine analytes, in buried core samples. Using this model, an on-going collaboration is occurring with the Nevada Field Office to address their need for uranium detection in soils and groundwater.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* John Jones and Bruce Crow
*Collaborating Organization:* DOE-NV

## Biogeochemistry

### Project: 64907

*Title:* "Green" Biopolymers for Improved Decontamination of Metals from Surfaces: Sorptive Characterization and Costing Properties
*PI:* Dr. Brian H. Davison
*Institution:* ORNL



The abundant synthesis of biopolymers by algae (*Nostoc* sp. GSV40). [see Project #64907]

*Description:* Entered discussions with algal biomass producers at Hebrew University and Ben Gurion University, both of Israel, on selection and production of biopolymer. Inexpensive production of the biopolymers is essential for the ultimate application. We established contacts with several researchers and developers in growing algae in bulk. These include commercial demos of biosorption in the U.S. Collaborations in detail will need to wait for selection of a biopolymer and completion of preliminary proof-of-concept tests.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Elisha Ter-Or and Shosham Arad
*Collaborating Organization:* Hebrew University and Ben Gurion University

## Engineering Science

### Project: 55052

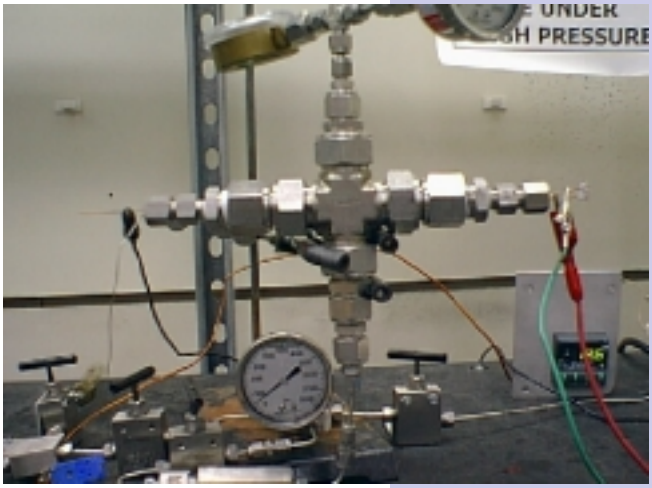
*Title:* Advanced Sensing and Control Techniques to Facilitate Semi-Autonomous Decommissioning
*PI:* Dr. Robert J. Schalkoff *Institution:* Clemson University

*Description:* The researchers for this project identified an end-user and began collaborations with the INEEL Decontamination, Decommissioning, and Remediation Optimal Planning System (DDROPS). The INEEL system has widespread applicability throughout DOE and is leading edge technology estimated to save the DOE millions of dollars. The goal is to incorporate EMSP's near real-time virtual reality modeling and imaging system as a component of the larger INEEL system.
*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Dick Meservey
*Collaborating Organization:* INEEL

### Project: 64979

*Title:* Basic Engineering Research for D&D of R.Reactor Storage Pond Sludge: Electrokinetics, Carbon Dioxide Extraction, and Supercritical Water Oxidation
*PI:* Dr. Edward A. Hamilton *Institution:* SCUREF

*Description:* Large quantities of mixed low level waste (MLLW) that fall under the Toxic Substances Control Act (TSCA) exist and continue to be generated at DOE sites across the country. Currently, the volume of these wastes is 23,500 m3, and the majority of these wastes (i.e., almost 19,000 m3) consists of PCBs and PCB-contaminated materials. Although a number of processes have been proposed for the recovery and/or destruction of these persistent pollutants, none has yet to emerge as the preferred choice for DOE cleanup. Recently, researchers at the INEEL indicated the possibility of previous DOE projects examining the use of SCWO to destroy chlorinated organics as a potential starting point for this project. Karen Moore of the INEEL will send a detailed list of literature references from the final project report on SWCO along with a copy of the final project report.
*Collaboration Type:* Program interaction
*Fiscal Year:* 2000
*Collaborator:* John Beller and Karen Moore
*Collaborating Organization:* INEEL



Electrochemical Cell at the University of South Carolina [see Project #64979]

*Description:* Collaborating researchers at the University of South Carolina (USC), Clemson University (CU), and the SRS (SRS) are investigating the fundamentals of a combined extraction and destruction process for the decontamination and decommissioning (D&D) of PCB-contaminated materials as found at DOE sites. Currently, the volume of PCBs and PCB-contaminated wastes at DOE sites nationwide is approximately 19,000 m3. While there are a number of existing and proposed processes for the recovery and/or destruction of these persistent pollutants, none has emerged as the preferred choice. Therefore, this research focuses on combining novel processes to solve the problem. The research objectives are to investigate benign dense-fluid extraction with either carbon dioxide (USC) or hot water (CU), followed by destruction of the extracted PCBs via either electrochemical (USC) or hydrothermal (CU) oxidation. Based on the results of these investigations, a combined extraction and destruction process that incorporates the most successful elements of the various processes will be recommended for application to contaminated DOE sites.

The SCUREF Project Director coordinates the activities of the three components of the research team, reviews bi-monthly progress reports, and conducts quarterly team meetings to share research results. The SRS component of the Project Team provides regulatory compliance information regarding PCB handling and usage, and provides model matrix material. This model material, used in the field to absorb PCB-contaminated liquids, will be contaminated in the lab and used for extraction experiments. The Savannah River Technology Center (SRTC) investigator will analyze matrix material that has been processed by SCUREF investigators for effectiveness of the extraction and destruction processes. In year three of the project, graduate students will spend a portion of the year on site performing experiments with PCBs under the supervision of the SRS team members. Also in year three, SRTC, using laboratory results provided by SCUREF investigators, will develop conceptual process designs for decontamination of PCB-contaminated matrices. The SRTC PI will evaluate these designs for technical and economic feasibility.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2000

*Collaborator:* Mike Matthews, David Bruce, Mark Thies, Lawrence Oji, John Pickett, Nancy Lowry

*Collaborating Organization:* Clemson University; University of South Carolina; Savannah River Technology Center; Facilities Decommissioning Division, WSRC.

*Description:* The INEEL has provided a detailed spreadsheet of all their PCB mixed wastestreams to provide the researchers a understanding of the maginitude of the problem. The INEEL also has offered to put the researcher in contact with wastestream owners if more information is required.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000

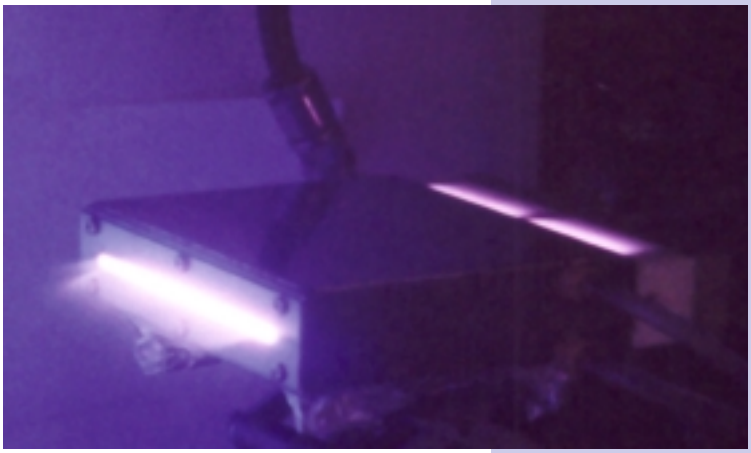
*Collaborator:* Mark Argyle

*Collaborating Organization:* INEEL

## Materials Science

### Project: 73835 (Renewal of Project 54914)

*Title:* Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces
*PI:* Dr. Robert F. Hicks *Institution:* University of California at Los Angeles



Front view of a 4" wide thermospheric-pressure plasma source operating with 750 Torr helium and 10 Torr oxygen. [see Project #73835, renewal of #54914]

*Description:* The researchers for this project have initiated collaborations with the INEEL and LANL and are directing their research towards specific needs at these end-user sites. The INEEL has provided the Atmospheric-Pressure Plasma Jet (APPJ) project with coupons coated with surrogate contamination allowing the researchers to evaluate the work in laboratory conditions. This project has wide spread application at all DOE sites with TRU contaminated buildings, equipment, or wastes. The goal of this technology is to remove TRU-contamination, allowing the contaminated waste to be treated as clean waste or to be re-classified to a lower level. This science is a dry application that generates very little secondary waste making it very appealing to any baseline processes.

*Collaboration Type:* Mission directed *Fiscal Year:* 2001
*Collaborating Organization:* INEEL and LANL

## Separations Chemistry

### Project: 60283

*Title:* Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation
*PI:* Dr. Michael J. Pellin *Institution:* ANL

*Description:* The waste stream generated in the D&D efforts for nuclear facilities includes a significant volume of material that is contaminated only in the surface or near-surface region. It is critical to understand the depth-dependent concentration and chemistry of radionuclide-contaminated surfaces. Complete removal and capture of the contaminated surface would greatly reduce the volume of waste material generated in, and thus the cost of, D&D efforts. This project represents the first detailed surface studies of the sorption of radionuclides in complex materials such as concrete. Collaboration is a joint interaction with Zawtech Inc. to do further research into areas of practical applications in industry.

*Collaboration Type:* Joint interaction *Fiscal Year:* 1999
*Collaborating Organization:* Zawtech Inc.

***Project: 64912***

*Title:* Improved Decontamination: Interfacial, Transport, and Chemical Properties of Aqueous Surfactant Cleaners

*PI:* Dr. David W. DePaoli *Institution:* ORNL

*Description:* This project is focused on surface decontamination using environmentally benign aqueous cleaners, specifically the removal of organic contaminants using surfactant solutions. Facilities throughout DOE have need for removal of organics (oils, PCBs, etc.) from solid substrates, particularly metals surfaces such as ductwork, pumps, tools, gloveboxes, etc. Aqueous-based solutions are attractive alternatives to chlorinated/fluorinated solvents that have been banned or are being phased out. They promise several advantages for decontamination processes, including low hazard potential, low cost, and reduced secondary waste volume. Laboratory-scale experimentation has been aimed at determining improved means for removal of organic contaminants using aqueous surfactant cleaners. We have found that the rate of oil removal can be significantly increased through a simple modification of process conditions. An invention based on our findings has been communicated, through a non-disclosure agreement, with a leading company that produces industrial cleaners. That company has agreed to collaboratively participate in testing of the technology through guidance and evaluation. Company representatives have arranged a visit to ORNL and the University of Tennessee on September 28, 2000 to evaluate the potential of the technology and to discuss partnership and commercialization.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2000

*Collaborating Organization:* ORNL/ University of Tennessee

*Description:* Work is currently being done with Dick Meservey and Amy Mikkola of the "New Idaho Large-scale Decontamination and Decommissioning Project" at the Idaho Engineering and Environmental Laboratory to identify specific site applications, perform bench-scale testing, and evaluate feasibility for incorporation into large-scale demos. The understanding developed in this work will be directly applied to decontamination/decommission tasks by testing surface samples from DOE contaminated sites (such as those from the enrichment process building of K-25 site) and will provide the basis for improved approaches for removal of organic contamination by synthetic surfactants. These improvements will lead to decreased hazards for workers, decreased secondary waste generation, increased efficiency, and lower cost. The proposed research program is a multi-disciplinary and multi-*Institution*al collaboration between a national laboratory and a university. The team includes engineers and scientists with expertise in colloid and interfacial phenomena and separation processes.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001

*Collaborator:* Dick Meservey and Any Mikkola

*Collaborating Organization:* INEEL

*Description:* We have an alliance with Petroferm Inc. of Fernandina Beach, Florida (A leader in industrial oil/grease removal technology) and are at the point of demonstrating our advanced technologies; our primary contact there is Dr. Nelson E Prietro (Technical Director). Petroferm is very interested in the general industrial applications in addition to D&D applications. We are currently involved with discussions on commercialization of the technology as well as additional laboratory and theoretical exploration. Current technology is focused on metal components that may be submerged in water-filled tanks. His use for the current technology is slightly different that we envisioned at the beginning of our research.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Dr. Nelson E Prietro
*Collaborating Organization:* Petroferm Inc.

## HEALTH/ECOLOGY/RISK

### Health Science

#### Project: 54546

*Title:* Engineered Antibodies for Monitoring of Polynuclear Aromatic Hydrocarbons
*PI:* Dr. Alexander E. Karu *Institution:* University of California at Berkeley

*Description:* The objective of this project is to use molecular biological techniques to derive a set of antibodies with useful affinities and selectivities for recovery and detection of polynuclear aromatic hydrocarbons (PAHs) in environmental and biological samples. The long-term goal is to develop immunodetection methods that will be useful in biomarker research and regulatory monitoring of PAHs. This project has established a collaboration with Dr. Tuan Vo-Dinh at ORNL to identify a sensor system and perform a demonstration.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborator:* Dr. Tuan Vo-Dinh
*Collaborating Organization:* ORNL

#### Project: 54684

*Title:* Mechanism Involved in Trichloroethylene-Induced Liver Cancer: Importance to Environmental Cleanup
*PI:* Dr. Richard J. Bull *Institution:* PNNL

*Description:* EPA is using the data we have generated and a paper describing the mode of action for induction of liver tumors to revise their risk assessment on trichloroethylene. EPA continues to track our published results as this decision process reaches its conclusions. A separate step will be actions taken under the Office of Water to revise drinking water standards or CERCLA to modify clean-up standards that are derived from the revised risk assessments.

*Collaboration Type:* Consulting *Fiscal Year:* 1998
*Collaborating Organization:* EPA

### Project: 55410

*Title:* Determining Significant Endpoints for Ecological Risk Analysis
*PI:* Dr. Thomas G. Hinton *Institution:* Savannah River Ecology Laboratory

*Description:* Protection of the environment from ionizing radiation, and the associated questions we are addressing through the EMSP program, are of national and international interest. We were asked to present our results and provide guidance at two important meetings. Nationally, the DOE is formulating guidance on how to conduct ecological risk anlayses through their Biota Dose Assessment Committee. Dr. Hinton asked to review their documents, and present our research results at a meeting in Aug. 1999. At the international level, Dr. Hinton was asked to be on a panel of experts at an International Atomic Energy Agency meeting in Vienna, Austria (Aug. 2000).

We addressed the issue of what are the appropriate endpoints when conducting ecological risk analyses, and whether or not the environment is automatically protected when exposures are limited to the point that humans are protected.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborating Organization:* International Atomic Energy Agency

*Description:* Our interest is in obtaining a scientifically defensible endpoint for measuring ecological risks to populations exposed to chronic, low-level radiation, and radiation with concomitant exposure to chemicals. To do so, we believe that we must understand the extent to which molecular damage is detrimental at the individual and population levels of biological organization. Ecological risk analyses based on molecular damage, without an understanding of the impacts to higher levels of biological organization, could cause cleanup strategies on DOE sites to be overly conservative and unnecessarily expensive. The PI has taken knowledge gained from this research and used it in his work with the DOE Biota Dose Assessment Group (BDAG). BDAG is currently reviewing ecological risk concepts and establishing guidelines for conducting ecological risks on DOE Facilities.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Dr. Thomas Hinton
*Collaborating Organization:* Savannah River Ecology Lab - University of Georgia

### Project: 60037

*Title:* Estimation of Potential Population Level Effects of Contaminants on Wildlife
*PI:* Dr. James Loar *Institution:* ORNL

*Description:* Although risk managers for CERCLA sites are concerned with risks to wildlife populations, methods for wildlife risk assessments are based on effects on individuals. The purpose of this project is to provide DOE with methods to assess risks to wildlife populations. In support of program objectives, a series of conference call meetings were held with these individuals to utilize their expertise in various areas.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* John D. Eisemann/ Rick Bennett/ Pierre Mineau/ Bruce Hope/ Clarence Callahan & Ned Black/ Regina Donahoe/ Jim Polinski/ Nathan Schumaker
*Collaborating Organization:* Nat. Wldlf. Res. Ctr. (USDA APHIS)/ Wldlf. Toxic., EPA Dul. Lab./ Can. Wldlf. Serv./ Ecorisk, Oregon Dept. of Env. Qual./ CA state regs./ EPA Reg. 9/ CA. Off. Env. Health Haz. Ass./ CA Dept. of Toxic Subs. Control/ EPA, Corvallis, OR.

### *Project: 73942 (Renewal of Project 59918)*

*Title:* Improved Radiation Dosimetry Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites
*PI:* Dr. Bobby R. Scott *Institution:* Lovelace Biomedical & Environmental Research Institute

*Description:* Additional data on lung cancer induced in Mayak workers exposed by inhalation to both plutonium and cigarette smoke were acquired by Dr. Scott from scientists at the Branch No. 1 of the Institute of Biophysics, Ozersk Russia. The data will facilitate making conclusions about possible interactions between alpha radiation and cigarette smoke in the induction of lung cancer. The data will also allow for additional insights to be made related to the validity of the linear, no-threshold hypothesis for cancer induction.
*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborator:* Unknown
*Collaborating Organization:* Branch No. 1 of the Institute of Biophysics, Ozersk Russia

*Description:* We are now assisting staff at the Rocky Mountain Remediation Services, L.L.C., Rocky Flats Environmental Technology Site in preparing a scientifically valid approach to selecting respiratory protection devices for use in very high concentrations of plutonium. Some concentration of interest would essentially lead to early occurring or delayed deaths without adequate worker protection. The activities at Rock Flats relate to decontamination and decommissioning. Our staff reviewed an original draft white paper related to selecting appropriate respiratory devices and major shortcomings related to protecting DOE decontamination/decommissioning workers were pointed out. We will continue to assist in preparing a more credible plan for protecting workers and in preparing an associated white paper.
*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Rocky Mountain Remediation Services, L.L.C.,
*Collaborating Organization:* Rocky Flats Environmental Technology Site

*Description:* The Department of Energy has standards that require evaluating non-cancer-producing radiological doses to the immediate worker in order to know the intake level that corresponds to serious injury or prompt death.

Historically, only criticality prompt doses have been calculated and characterized as high, moderate, or low. Doses associated with inhalation intakes have not been adequately evaluated. Rather, they have only been subjectively indicated as high, moderate, or low, with little scientific justification. Rocky Flats Environmental Technology Site (RFETS) scientists are faced with evaluating intakes of plutonium aerosols that would be associated with serious radiation deterministic effects (e.g., respiratory dysfunction, death from radiation pneumonitis), following a plutonium (Pu) accident involving inhalation exposure. Such accidents could arise during decommissioning/deactivation operations related to Pu-contaminated facilities. Researchers have assisted RFETS scientists in evaluating risks to RFETS workers for radiation-induced deterministic effects in the lung associated with accident scenarios related to inhaling mixtures of Pu-238, Pu-239, Pu-240, Pu-241, and Am-241. These mixtures arise for weapons-grade Pu, aged weapons-grade Pu, and high Am-241 residue that contains Pu. The normalized-dose risk model developed by Dr. B. R. Scott for radiation-induced deterministic effects was used. Variability and uncertainty were accounted for via the use of distributions for model parameters previously published by Dr. Scott. Results indicate that milligram quantities of mixtures involving the indicated isotopes must be inhaled in order to produce deterministic effects in the lung. The cited intake includes inhaled material that is not deposited in the respiratory tract. However, rather than occurring promptly, the deterministic effects may occur months to years after inhaling the Pu/Am, as threshold radiation dose for deterministic effects may not be reached until such times after inhalation exposure.

*Collaboration Type:* Consulting *Fiscal Year:* 2001
*Collaborator:* Dr. Vern L. Peterson
*Collaborating Organization:* Rocky Flats Environmental Technology Site

*Description:* For years, there has been concern about possible harm to the general public from plutonium (Pu) contamination at the U.S. Department of Energy's Rocky Flats Environmental Technology Site. Until recently, little information was available on Pu risks based on actual human exposure to Pu isotopes. Lung cancer risks estimates for humans that inhale Pu therefore are based largely on extrapolations from animal studies or extrapolations from experience with external radiations (e.g., atomic bomb survivors) or on persons exposed to radon. Now it is known that the radiation dose from radon is spread differently over the lung than is the case for Pu aerosols; thus, risks estimates based on radon are inappropriate for Pu aerosols. With partial support from EMSP Project 59918, a joint Russian/U.S. case-control study of lung cancer induction by inhaled Pu-239 plus gamma rays, as well as cigarette smoke, has been conducted, which provides new insights about pair-wise interactions of the indicated three factors in lung cancer induction. Dr. Z. B. Tokarskaya of the First Institute of Biophysics, Ozersk Russia, headed the study. The database used relates to Mayak plutonium production facility workers in the Chelyabinsk region of Russia. The study included 486 individuals (162 cases), with matching of 2 controls per case. Three

levels of smoking were considered: low (controls), middle, and high. Using odds-ratio methods to investigate pair-wise interactions, synergistic interactions were demonstrated for radiation (gamma dose or Pu-239 body burden) plus high levels of smoking. Otherwise additive effects could not be ruled out for smoking and radiation. However, combined exposure to external gamma rays and Pu-239 caused a dramatic synergistic interaction, which is consistent with threshold-type risk vs. dose relationships for radiation. Although these results are preliminary, demonstration of a threshold for Pu-induced lung cancer could significantly alter cleanup criteria for Pu-contaminated sites such as Rocky Flats.

*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* Dr. Z. B. Tokarskaya
*Collaborating Organization:* First Institute of Biophysics (FIB-1) Ozersk, Russia

### *Project: 74050 (Renewal of Project 59882)*

*Title:* Measurement of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational and Environmental Exposure at US DOE Fernald
*PI:* Dr. Naomi H. Harley *Institution:* New York University Medical School

*Description:* One objective of this project is to develop the sequential radiochemistry necessary to measure any environmental sample for the isotopes of uranium, thorium, radium, and lead-210. To utilize this radiochemistry for lead-210 before and after the radium is removed form the silos to accurately determine the amount of radon gas released, from the parent radium during removal. To utilize the radiochemistry to accurately trace and delineate thorium, radium, and uranium nuclides, originating from Fernald, in the environment. Dr. Fisenne at DOE Environmental Measurements Laboratory has developed a sequential radiochemical procedure to analyze any environmental sample matrix, presently focused on Soil samples, for Lead-210, radium, thorium, and uranium isotopes. We are currently cunsulting with Dr. Fisenne.

The insides of the radon-222, radon-220 monitor device. [see Project #74050, renewal of #59882]

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Dr. Isabel Fisenne
*Collaborating Organization:* Environmental Measurements Laboratory

### *Low Dose Radiation*

#### *Project: 69904*

*Title:* Low-Dose Risk, Decisions, and Risk Communication
*PI:* Dr. James Flynn *Institution:* Decision Science Research Institute

*Description:* Science and Risk at the Community Level: Three Case Studies - A social research project on science and risk information roles in guiding the attitudes, opinions, perceptions and preferences of community-level residents. In a joint effort we have conducted preliminary examination of 14 potential communities located near DOE and nuclear power generating facilities. Three communities have been chosen for in-depth studies. Fieldwork in these three communities is now underway.
*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* S. Tuler, T. Webler, and J. Wilhoit
*Collaborating Organization:* Decision Research and the Social and Environmental Research Institute

*Description:* Decision Research sponsored a three-day workshop held in Eugene, Oregon, June 12-14, 2000. The event brought together twenty researchers from 10 *Institution*s to examine the role of science and risk communication in presenting the results of the DOE Low Dose Radiation Research Program. A transcript of the Workshop proceedings is posted at the Decision Research web site: www.decisionresearch.org.
*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* A. Brooks, R. Kasperson, S. Tuler, W. Freudenburg, S. Friedman, B. Wynne, J. Kasperson, N. Pidgeon, E. Omohundro, D. Lash, S. Johnson
*Collaborating Organization:* Washington State University; Clark University; The Social and Environmental Research Institute; University of Wisconsin, Madison; Lehigh University; Lancaster University (UK); Oregon State University; University of East Anglia (UK); University of Oregon

#### *Project: 69906*

*Title:* Markers of the Low-Dose Radiation Response
*PI:* Dr. William S. Dynan *Institution:* Medical College of Georgia

*Description:* We seek to develop a technology that will allow direct visualization of DNA double-strand break repair complexes in their original places in the nuclei of irradiated cells. These studies will help bridge the gap between biochemical studies of repair enzymes and an understanding of the process of repair as it actually occurs within the radiation-injured cell. We have made new plans to collaborate with Dr. Thomas Orlando, who is developing a new type of inexpensive micro-irradiation probe. We will irradiate single cells and study the effect on our markers both in the target cells and in bystander cells.
*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Dr. Thomas Orlando
*Collaborating Organization:* Georgia Institute of Technology

# HIGH-LEVEL WASTE

## Actinide (Heavy Element) Chemistry

### Project: 65398

*Title:* Characterization of Actinides in Simulated Alkaline Tank Waste Sludges and Leach Solutions

*PI:* Dr. Kenneth L. Nash *Institution:* ANL

*Description:* Our project investigating the chemistry of actinides in strongly alkaline media continues to make progress on understanding the behavior of actinides in alkaline solutions and sludge simulants. We were recently contacted by the SRS inquiring after our observations regarding the behavior of uranium during the washing of PUREX sludge simulants in connection with some work they are involved in regarding waste tank remediation. SRS has some solid material that may contain moderate concentrations of enriched uranium. Their concern is to make certain that they won't accidentally assemble a critical mass during this dissolution procedure. Their inquiry specifically targeted the solubility limits for uranium in alkaline solutions, which we indicated based on the results of our EMSP project to be in the range of 1-2 x 10-5 M, in general agreement with literature predictions (based on information obtained under somewhat different conditions). Our observations essentially confirmed their expectations.

*Collaboration Type:* Consulting *Fiscal Year:* 2001

*Collaborator:* David Hobbs

*Collaborating Organization:* SRS

## Analytical Chemistry & Instrumentation

### Project: 55318

*Title:* Improved Analytical Characterization of Solid Waste Forms by Fundamental Development of Laser Ablation Technology

*PI:* Dr. Richard E. Russo *Institution:* LBNL

*Description:* Characterization continues to be a need within the DOE EM program in the areas of high-level waste, tanks, sub-surface contaminant plumes, D&D activities, spent nuclear fuel, mixed wastes, and plutonium disposition. Laser ablation can provide direct characterization of any solid waste form in a timely manner and at a reduced cost compared to conventional analytical dissolution procedures. The primary technical difficulties hindering this technology are matrix dependence and fractionation, both effect accuracy of quantitative characterization. These issues must be understood on a fundamental level to develop laser ablation as a routine characterization technology. Understanding these fundamental issues is the basis of the EMSP project. The PI has established an interaction with the primary personnel responsible for setting up the laser ablation inductively coupled plasma - mass spectroscopy (LA-ICP-MS) system in Building 222S at PNNL. The PI has visited the Hanford Site and toured the LA facility.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* John Hartman, Mike Alexander, and Monte Smith
*Collaborating Organization:* PNNL

*Description:* DOE Materials Disposition Program is developing two LA systems, at SRS and LLNL for Pu characterization. Because of the reputation of the PI and the EMSP program, Russo was asked to help develop the systems and standards for this PuO2 effort.
*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* Chris Bannochie
*Collaborating Organization:* DOE Savannah River

*Description:* This project has continuing interaction with other EMSP investigator studying laser ablation. This includes projects 55205 - A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals, and 60283 - Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation.
*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Dr. Scott Goode and Dr. Michael J. Pellin
*Collaborating Organization:* University of South Carolina and ANL

### *Project: 60075*

*Title:* Particle Generation by Laser Ablation in Support of Chemical Analysis of High Level Mixed Waste from Plutonium Production Operations
*PI:* Dr. J. Thomas Dickinson *Institution:* Washington State University

*Description:* Methods for compositional analysis of fissile materials and radioactive/ toxic wastes are being developed to support characterization prior to treatment and remediation. The need for rapid, real-time, on-site characterization of waste at DOE sites has led to deployment of laser ablation-inductively coupled plasma mass spectroscopy (LA/ICP-MS) systems for elemental and isotopic analysis at several locations, including Hanford, Los Alamos, and the INEEL. These systems can provide qualitative or semi-quantitative analysis of certain sample types with minimal sample handling. Research into the fundamental physical processes of particle formation during laser ablation is required to provide basic understanding that will allow us to maximize the utility of these systems. As such, an on-going collaboration is occurring with the Nevada Field Office to address their need for uranium detection in soils and groundwater.
*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* John Jones and Bruce Crow
*Collaborating Organization:* DOE-NV

*Description:* We have been working with Dr. Beverly Crawford. Dr. Crawford is in charge of a laser ablation ICP-MS system that has been installed in a hot cell in the Hanford 222S building. One of the key technical questions is how well laser ablation can determine the overall bulk composition of a

heterogeneous sample given a small volume of material sampled. We have begun to address the homogeneity issue.

*Collaboration Type:* Joint interaction *Fiscal Year:* 1999
*Collaborator:* Jim Rindfleisch
*Collaborating Organization:* Long Range Waste Management Program, INEEL

*Description:* Performing laser ablation/description analytical determination on a surrogate sample. Contacted Arlin Olson and Scott Herbst to identify the surrogate and analytical requirements. Investigate analysis of these samples by laser ablation IMP-MS as well as a related method, laser desorption mass spectroscopy to determine key molecular components. The goal is to generate a complete mass balance of the calcine waste.

*Collaboration Type:* Joint interaction *Fiscal Year:* 1999
*Collaborator:* Dr. Beverly Crawford
*Collaborating Organization:* Numatec, Hanford

### Project: 60219

*Title:* Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Liquid Waste
*PI:* Dr. Digby D. MacDonald *Institution:* Pennsylvania State University

*Description:* The principal goals of this project are to develop advanced electrochemical emission spectroscopic (EES) methods for monitoring the corrosion of carbon steel in simulated DOE liquid waste and to develop a better understanding of the mechanisms of the corrosion of metals and alloys in these environments. To faciliate this goal, interaction with SRI International has been begun.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2000
*Collaborator:* Dr. George Engelhardt
*Collaborating Organization:* SRI International

### Project: 65435

*Title:* Millimeter-Wave Measurements of High Level and Low Activity Glass Melts
*PI:* Dr. Paul P. Woskov *Institution:* Massachusetts Institute of Technology

*Description:* Laboratory experiments at MIT have established the feasibility for real-time monitoring of all thee parameters, temperature, conductivity, and viscosity. Also a new capability for molten glass density measurements at high-temperature was discovered. A key milestone in the second year was a meeting with Tank Focus Area representatives at MIT on December 7, 1999, to discuss monitoring priorities and the transfer of this technology to TFA.

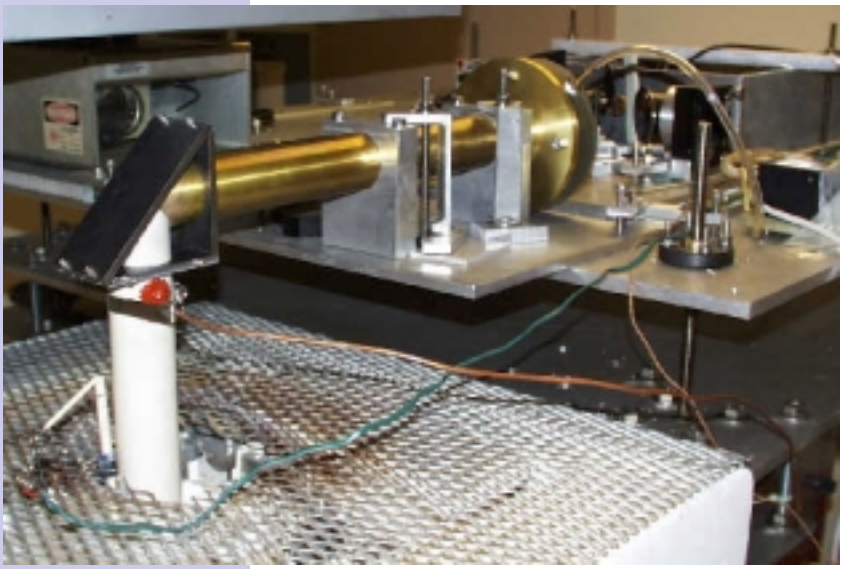
*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Bill Holtzcheiter, Frank Thomas III, from SRTC; Tom Thomas, from INEEL; Glenn Bastiaans, from Ames; S. K.. Sundaram, from PNNL
*Collaborating Organization:* Tanks Focus Area

*Description:* The developments of this project are being closely monitored by the Tank Focus Area (TFA). A formal meeting with TFA representatives was held at Plasma Science Fusion Center, Massachusetts Institute of Technology on December 7, 1999 to discuss the transfer of the millimeter-wave-based melter diagnostics technology being developed under the EMSP project (PNNL-MIT-SRTC). The meeting was successful in identifying potential deployment of millimeter wave technology to meet the needs of the TFA. The participants of the meeting were as follows:

- PNNL - S. K. Sundaram
- MIT - Paul Woskov, Paul Thomas, Kamal Hadiddi, and John Machuzak
- SRTC - Bill Holtzcheiter, Frank Smith III
- Ames - Glenn Bastiaans
- INEEL- Tom Thomas

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborator:* (see description)
*Collaborating Organization:* (see description)

*Description:* The objectives of the project are to develop new real-time sensors for characterizing glass melts in high level waste (HLW) and low activity waste (LAW) melters, and to understand the scientific basis and bridge the gap between glass melt model data and melter performance. A basic goal is to characterize glass melts in-situ with the new diagnostic capability so that data will represent the actual melt's behavior. The work will be closely coupled to the needs of the Defense Waste Processing Facility, West Valley Demonstration Project, and vitrification efforts at Hanford, Oak Ridge, and Idaho sites. The project is a collaboration between the MIT Plasma Science and Fusion Center, PNNL, and the Savannah River Technology Center. In addition, discussions are in progress with Tom Thomas of the Tanks Focus Area regarding the possibility of demonstrating with the TFA.



Experimental setup for measuring the viscosity inside a melter. The represents the first time that a possibility for such a measurement has ever been demonstrated in real-time. Mullite waveguide shown going down into furnace with pressure sensor connection just below miter bend. Flanged window end of brass waveguide is connected to a hose for pressurizing waveguide with nitrogen when the mullite end of the waveguide is immersed in the glass. Millimeter-wave pyrometer electronics are inside the aluminum box in the background on right. [see Project #65435]

*Collaboration Type:* Program interaction
*Fiscal Year:* 1999
*Collaborator:* Tom Thomas
*Collaborating Organization:* Tanks Focus Area

*Description:* Collaborations with other laboratories are being exploited to field test the research accomplished by this project. For example, a field test at TFA request was carried out at the Clemson Environmental Technology Laboratory (CETL) in August 2000 on a pilot scale melt test of an INEEL glass surrogate. An open invitation exists from CETL for additional joint experiments. The EMSP support is thus leveraged by the field test facilities being provided by TFA.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborating Organization:* Tanks Focus Area

## *Engineering Science*

### *Project: 54656*

*Title:* Mixing Processes in High-Level Waste Tanks
*PI:* Dr. Per F. Peterson *Institution:* University of California at Berkeley

*Description:* Flammable gases can be generated in DOE high-level waste tanks. This project is a concentrated effort to develop models and a numerical tool to mechanistically predict mixing processes in large waste-tank volumes, where mixing processes can be driven by hot and cold vertical and horizontal surfaces and injected buoyant jets. General Electric is funding a doctoral student to work on this project.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborating Organization:* General Electric

### *Project: 60143*

*Title:* Foaming in Radioactive Waste Treatment and Immobilization Processes
*PI:* Dr. Darsh T. Wasan *Institution:* Illinois Institute of Technology

*Description:* The physical mechanisms of the formation of foam in radioactive waste treatment and waste immobilization processes are poorly understood. The objective of this research is to develop a basic understanding of the mechanisms that produce foaming, to identify the key parameters which aggravate foaming, and to identify effective ways to eliminate or mitigate foaming. We are working with Savannah River Salt Processing Project to help evaluate and select optimal foaming agent to mitigate foaming problems that occurred in the Small Tank Tetraphenylborate Precipitation (STTP) program.

*Collaboration Type:* Consulting *Fiscal Year:* 2001
*Collaborating Organization:* Savannah River Salt Processing Project and Tanks Focus Area

*Description:* Illinois Institute of Technology (IIT) has been working closely with the Savannah River Technology Center in the development of an improved antifoaming agent for the Defense Waste Processing Facility (DWPF). The key to the development of this new antifoam agent was a close working relationship between the IIT researchers and the customer (Dan

Lambert) at the SRS (SRS). University and national lab researchers often come up with unique and innovative solutions that are useless to the customer. The reason for the success of this project can be attributed to the fact that the IIT researchers sought to understand the science and the limitations in the customer's waste processing facility through close working relationships.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborating Organization:* Savannah River Technology Center

## Geochemistry

### Project: 60403

*Title:* Phase Chemistry of Tank Sludge Residual Components
*PI:* Dr. James L. Krumhansl *Institution:* Sandia National Laboratories - Albuquerque

*Description:* Because it is not possible to recover all of the contaminated sludge from the bottoms of decommissioned waste storage tanks, a credible model for the release of radionuclides from residual sludge is needed. Those sludge components most likely to retain radionuclides will be identified and synthesized. Radionuclide sorption and desorption will also be studied. AFM and STM studies will provide a firm atomistic explanation for the observed interactions between the sludge, solutions, and radionuclides. This understanding will be used to develop a quantitative radionuclide release source term for use in the performance assessment calculations.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Larry Bustard
*Collaborating Organization:* TFA

## Inorganic Chemistry

### Project: 65411

*Title:* Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes
*PI:* Dr. Jun Liu *Institution:* PNNL

*Description:* Aluminum-containing phases represent the most prevalent solids that can appear or disappear during the processing of radioactive tank wastes. Of all constituents of tank waste, Al-species have the greatest potential for clogging pipes and transfer lines, fouling highly radioactive components such as ion exchangers, and completely shutting down processing operations. The primary focus of this project is to understand the major factors controlling precipitation, scale formation, and cementation of existing soluble particles by Al-containing phases. The results will be used to predict and control precipitation, scale formation, and cementation under tank waste processing conditions. The results will also provide information regarding what Al-containing phases form and how soluble such phases are in basic tank waste solutions. The project will have an important impact on waste minimization and on the retrieval, transport,

and separation of tank wastes. Collaboration with Dr. Albert Hu at Lockheed Martin Hanford Company to perform simulations to support the ESP modeling work at Hanford.

*Collaboration Type:* Program interaction *Fiscal Year:* 1999
*Collaborator:* Dr. Albert Hu
*Collaborating Organization:* Lockheed Martin Hanford Company

### *Project: 73778 (Renewal of Project 60296)*

*Title:* Research Program to Investigate the Fundamental Chemistry of Technetium
*PI:* Dr. David K. Shuh *Institution:* LBNL

*Description:* This project addresses the fundamental solution chemistry of technetium (Tc) in the waste tank environment, and the stability of Tc in various waste forms. A separate facet of this project is the search for lower valent forms of Tc that may be incorporated in various waste forms for long term storage. Collaborated with PNNL as a participant (technical expert) at Technetium Chemistry workshop review panel assessing tank technetium removal/disposition options.

*Collaboration Type:* Consulting *Fiscal Year:* 1998
*Collaborating Organization:* PNNL

### *Project: 73832 (Renewal of Project 55229)*

*Title:* The NOx System in Homogeneous and Heterogeneous Nuclear Waste
*PI:* Dr. Dan Meisel *Institution:* University of Notre Dame

*Description:* This project, a collaborative ANL/PNNL effort, studies processes of the title system as it relates to the chemistry in high level liquid nuclear waste (HLW). The program is structured to transfer the information directly to the Hanford site operators (via "Organic Aging Studies, *PI:* Don Camaioni, PNNL). Our activity is also closely coordinated with another EMSP project ("Interfacial Radiolysis", *PI:* Thom Orlando, PNNL) and we include below our results that relate directly to that project. We determined the redox potential of the NO32- radical and its possible conversion to NO radical rather than to NO2. We also determined the redox potential of the analogous NO22- radicals because this parameter will determine whether such a conversion is possible. We concluded that both NO2 and NO radicals are important intermediates in HLW and the relative importance will depend on the concentration of nitrite in the waste tank. As a consequence we will coordinate our activity with a recently awarded EMSP project that focuses on NO chemistry and its derivatives ("Reactivity of Peroxynitrite", *PI:* Sergei Lymar, BNL).

*Collaboration Type:* Mission directed *Fiscal Year:* 1999
*Collaborator:* Sergei Lymar, Thom Orlando
*Collaborating Organization:* BNL, PNNL

## Materials Science

### Project: 60020

*Title:* Stability of High-Level Waste Forms
*PI:* Dr. Theodore M. Besmann *Institution:* ORNL

*Description:* Models of phase relations and liquidus temperatures developed in this EMSP program are being used to evaluate test results from the Tanks Focus Area Immobilization Program Waste Loading Improvements in High and Low Activity Glasses and Waste Form Product Acceptance Testing. The focus at this time is on conditions where crystallization occurs in glass processing. By applying models to the test data, an understanding of crystallization and how to avoid it may be obtained.
*Collaboration Type:* Joint interaction *Fiscal Year:* 1999
*Collaborator:* John Vienna
*Collaborating Organization:* PNNL

*Description:* Experimental studies of phase relations in the sodium oxide-boron oxide-uranium (VI) oxide system are being run in this EMSP program because there is no information in the literature. This data is needed for modeling actinide behavior in glasses. The results of these tests are also being spun off to assist the Uranium-233 Disposition Program of the Office of Fissile Materials Disposition (DOE/MD). They are considering dissolution of uranium oxide in sodium borate or boron oxide as an option for Uranium-233 disposition. As experimental data is produced, it is made available to the Uranium-233 Program to assist in their development of a flow sheet. Because of the dearth of information on this system, it is not surprising that any information that is produced may be applied in different activities.
*Collaboration Type:* Joint interaction *Fiscal Year:* 1998
*Collaborator:* Charles Forsberg
*Collaborating Organization:* ORNL

*Description:* We have supported efforts on increasing waste loading in glass. We performed computations modeling a waste glass formulation to predict precipitation of a crystalline phase, nepheline, which destabilizes the glass.

Based on this work a compositional maps at different temperatures indicating ranges under which nepheline is likely to precipitate was developed. We also produced liquidus temperature plots as a function of composition. Results indicates that nepheline formation can be suppressed at high silica and/or boria contents.
*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* John Vienna, Pavel Hrma and Hong Li
*Collaborating Organization:* Tanks Focus Area Immobilization Project Waste Loading Optimization Task; PNNL

*Description:* The objective of the project is to use a new approach to develop solution models of complex waste glass systems and spent fuel that are predictive with regard to composition, phase separation, and volatility. We have been

supporting efforts on increasing waste loading in glass. We have performed computations modeling a waste glass formulation to predict precipitation of a crystalline phase, nepheline, which destabilizes the glass. The results indicated compositional regions that promoted or suppressed precipitation. These can be used to help design glass compositions that will allow increased waste loading.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* John Vienna, Pavel Hrma, and Hong Li
*Collaborating Organization:* TFA Immobilization Project (PNNL)

### *Project: 60362*

*Title:* Ion-Exchange Processes and Mechanisms in Glasses
*PI:* Dr. B. Peter McGrail *Institution:* PNNL

*Description:* The objective of this project is to develop an understanding of the processes and mechanisms controlling alkali ion exchange and to correlate the kinetics of the ion-exchange reaction with glass structural properties. The fundamental understanding of the ion-exchange process developed under this study will provide a sound scientific basis for formulating low exchange rate glasses with higher waste loading, resulting in substantial production and disposal cost savings.

*Collaboration Type:* Program interaction *Fiscal Year:* 1999
*Collaborator:* D.K. Shuh
*Collaborating Organization:* LBNL

### *Project: 65408*

*Title:* Mechanisms and Kinetics of Organic Aging in High-Level Nuclear Wastes
*PI:* Dr. Donald M. Camaioni *Institution:* PNNL

*Description:* Highly radioactive wastes stored at Hanford and Savannah River DOE sites have unresolved questions relating to safety of the stored waste, as well as needs for safe, effective, and efficient waste processing to minimize the volume of high-level waste (ULW) streams for disposal. Dr. Camaioni has supplied technical input on tank waste issues to Hanford Site contractor personnel. Discussions with CH2M Hill Hanford Group, Inc. regarding the chemistry of polychlorinated biphenyls in Hanford tank wastes have taken place. DOE is interested in knowing the extent to which PCBs may undergo radiation and chemical destruction.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* Joe Meacham
*Collaborating Organization:* CH2M Hill Hanford Group, Inc

### *Project: 73748 (Renewal of Project 60345)*

*Title:* New Metal Niobate and Silicotitanate Ion Exchagers: Development and Characterization
*PI:* Dr. Mari Lou Balmer *Institution:* PNNL

*Description:* Research performed on this EMSP project has led to a mission-directed, joint interaction between researchers on this program and end users of the CST at SRS. EMSP principal investigators at PNNL and SNL have

been asked to evaluate the effect of temperature excursions (below 120 °C) on the performance and material properties of the CST. This information will be used by DOE to select the best process for Cs separation at SRS. In addition, the data provided by PNNL and SNL will be used to develop engineering solutions process upsets that result in minor temperature excursions. This is an EM-funded program.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborating Organization:* CST and SRS

*Description:* The Tanks Focus Area is managing the research and development program for the Salt Processing Project at the SRS. Three candidate cesuim removal technologies are being considered for down selection: Crystalline Siliconate Non-Elutable Ion Exchange (CST), Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipation (STTP). The research conducted under this EMSP project is directly applicable to the CST process. The principal investigator for this project is being funded by the Tanks Focus Area to bring their expertise and creativity to the development and selection process for this critical DOE project.

*Collaboration Type:* Consulting *Fiscal Year:* 2001
*Collaborating Organization:* Savannah River Salt Processing Project and Tanks Focus Area

*Description:* This project, a collaborative PNNL/SNL/UC Davis effort, identifies new waste forms and disposal strategies specific to crystalline silicotitanate (CST) secondary waste that is generated from Cs and Sr ion exchange processes. The goals of the program are to reduce the costs associated with CST waste disposal, to minimize the risk of contamination to the environment during CST processing, and to provide DOE with technical alternatives for CST disposal. The technical objectives of the proposed work are to fully characterize the phase relationships, structures, and thermodynamic and kinetic stabilities of crystalline silicotitanate waste forms and to establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry. Collaborations for each associated task are as follows:

Task: Evaluation of thermally converted CST and structure/properties relationship studies of silicotitanates and related compounds.

- Y. Su, E. Bitten, and D. McCready, PNNL (Program interaction).

Task: Hydrothermal synthesis silicotitanates and related ion exchanger material.

- Nenoff and M. Nyman, SNL (Program interaction).

Task: Thermochemical studies of silicotitanates and related ion exchanger materials.

- A. Navrotsky and H. Xu, UC Davis (Program interaction).

Task: Single crystal growth.

- Dr. R. Roth, NIST and The Viper Group (Consulting).

Task: Radiation damage studies of silicotitanates.

- Professor R. Ewing, University of Michigan (Consulting).

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* (see description)
*Collaborating Organization:* (see description)

*Description:* In this program, we at SNL have developed both a silicotitanate ion exchanger and a new Metal Niobate Ion exchanger. Both are excellent at divalent cation selectivity. The Metal Niobate Ion Exchanger shows exceptional selectivity for divalent cations over monovalent cations. Though this is in the experimental stage (and NOT yet an optimized material), we do see great potential for this material is a variety of applications around the DOE complex. This material is currently submitted for a patent. We are in discussions with INEEL, about simulant testing of these non-optimized materials for various DOE complex wastes.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborator:* Dean Peterman
*Collaborating Organization:* INEEL

### *Project: 73750 (Renewal of Project 54672)*

*Title:* Radiation Effects in Nuclear Waste Materials
*PI:* Dr. William J. Weber *Institution:* PNNL

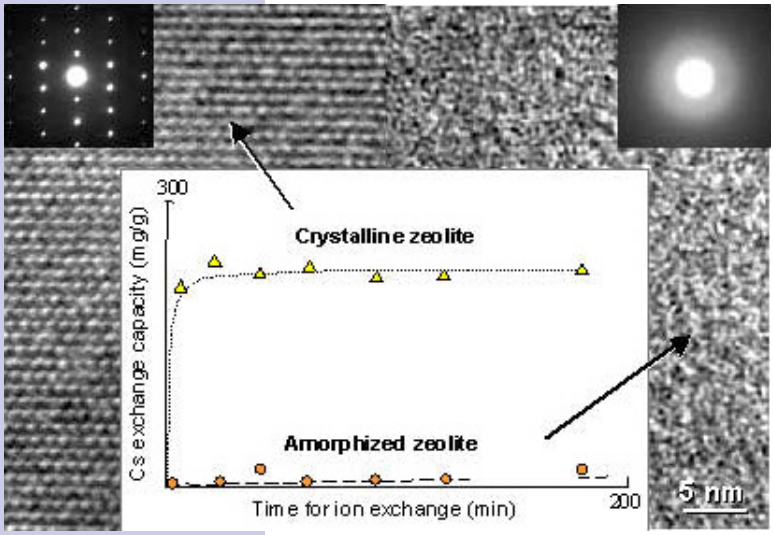
*Description:* The PI was requested to assist in evaluating potential radiation-induced failure of protective glass globes for lights in the in-tank camera systems for Tank 101-SY at Hanford. Unexplained failure of two globes had raised some safety concerns. Working with Lockheed Martin Hanford Co. staff, an interim testing program was designed for the protective glass globes, a procedure to minimize potential failure (change globes frequently) was advised, and some preliminary measurements and evaluations were conducted on irradiated globes. No permanent solution was developed as of yet.

*Collaboration Type:* Consulting *Fiscal Year:* 1998
*Collaborator:* Scott M Werry
*Collaborating Organization:* Lockheed Martin Hanford Co.

### *Project: 73762 (Renewal of Project 54691)*

*Title:* Radiation Effects on Sorption and Mobilization of Radionuclides during Transport through the Geosphere
*PI:* Dr. Lu-Min Wang *Institution:* University of Michigan

*Description:* Successful, demonstrated containment of radionuclides in the near-field can greatly reduce the complexity of the performance assessment analysis of a geologic repository. The chemical durability of the waste




Effect of solid-state amorphization on Cs exchange capacity of zeolite. As demonstrated by University of Michigan, zeolite lost 95% of its Cs exchange capacity after solid-state amorphization. [see Project #73762, renewal of #54691]

form, the corrosion rate of the canister, and the physical and chemical integrity of the back-fill provide important barriers to the release of radionuclides. However, near-field containment of radionuclides depends critically on the behavior of these materials in a radiation field. Continued efforts in this regard include the evaluation of the capabilities of the uranyl phases to incorporate and retard release of important radionuclides: Np-237, Se-79, Tc-99, and I-129.

*Collaboration Type:* Program interaction
*Fiscal Year:* 2000
*Collaborator:* Professor Peter Burns
*Collaborating Organization:* Notre Dame

*Description:* The objective of this research program has been to evaluate the long-term radiation effects in materials used in processing high-level nuclear waste or materials in the near-field of a nuclear waste repository. This program has established the following collaborations:

Dr M. L. Balmer (PNNL) and Dr. T. M. Nenoff (SNL) - EMSP Project 60345

- We have studied radiation effects on samples associated with the development of new silicotitanate waste form development provided by their research groups and provided data to them.

Dr. G. Liu (ANL) - EMSP Project 55367

- Information and experience exchanged on radiation damage studies.

Prof. A. Clearfield (Texas A&A University) - EMSP Project 54735

- We have obtained silicotitanate samples synthesized by Prof. Clearfield and conducted a preliminary study on radiation effects in the sample.

Dr. W.J. Weber (PNNL) - EMSP Project 54672

- Information and experience exchange on radiation damage studies.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* (see descriptions)
*Collaborating Organization:* (see descriptions)

*Description:* The principal sources of radiation in high-level nuclear waste are ?-decay of the fission products (e.g., 137Cs and 90Sr) and ?-decay of the actinide elements (e.g., U, Np, Pu, Am and Cm). Both types of radiation can cause important chemical and physical changes in materials (e.g., in-

crease in leach rates, volume expansion, solid state radiolysis and bubble formation, and reduced cation exchange capacity). The radiation-solid interactions are complex because they involve a combination of ionization effects due to electronic excitations and ballistic effects due to elastic collisions. The strength of the radiation field decreases dramatically with time, and the type of radiation damage varies over time (?-decay damage due to actinides dominates over ?-decay effects due to fission products with increasing time due to the long half-lives of the actinides). Further, the radiation effects vary as a function of the type of solid (ionic vs. covalent), the type of damage (inelastic vs. elastic interactions), the temperature of the irradiation, and the kinetics of the annealing mechanisms. Ongoing collaborative work includes that accomplished with Peter Burns of Notre Dame University on the fate of fission products released by the corrosion and alteration of spent nuclear fuel.

*Collaboration Type:* Program interaction *Fiscal Year:* 1999
*Collaborator:* Professor Peter Burns
*Collaborating Organization:* Notre Dame

### *Project: 73976 (Renewal of Project 55110)*

*Title:* Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes
*PI:* Dr. Delbert E. Day *Institution:* University of Missouri-Rolla

*Description:* Drs. Bruce Bunker and Lou Balmer provided information for sludge compositions in various tank farms, especially for wastes considered good candidates for iron phosphate glasses. Iron phosphate glasses were provided to Dr. Bill Weber for radiation damage studies. Dr. Pavel Hrma provided useful data for borosilicate glasses.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Drs. Bruce Bunker, Lou Balmer, Bill Weber, & Pavel Hrma
*Collaborating Organization:* PNNL

*Description:* We are collaborating on a project whereby we are developing an iron phosphate glass containing INEEL waste (calcine) that will eventually be melted in the cold wall induction furnace in Russia. This collaboration is an important step in moving the interesting iron phosphate glasses out of the laboratory into the real world of “large scale” or practical production.

*Collaboration Type:* Mission directed *Fiscal Year:* 2001
*Collaborator:* Dirk Gombert
*Collaborating Organization:* INEEL

*Description:* Dr. William G. Ramsey provided information for sludge compositions and evaluated iron phosphate glasses which contained uranium and plutonium. Undergraduate and graduate students from UMR worked part time at the Savannah River Laboratory with Drs. Carol Jantzen, William Miller, and others.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Drs. William G. Ramsey, Carol Jantzen, & Wiiliam Miller
*Collaborating Organization:* Westinghouse Savannah River Company

*Description:* Certain high level wastes (HLWs) are not well suited for vitrification in borosilicate (BS) glasses because they contain components such as phosphates that are poorly soluble in a BS host matrix. The waste loading must be significantly reduced if one is to successfully vitrify such problematic wastes in a BS glass. Iron phosphate glasses offer a technically feasible and cost effective alternative to borosilicate glasses for vitrifying such HLWs. The main objective of the project was to investigate the atomic structure-property relationships, and glass forming and crystallization characteristics, of these iron phosphate glasses and glasses containing nuclear waste components. Other physical properties such as density and thermal expansion were studied. Collaborations for each associated task are as follows:

Task: X-Ray Absorption Spectroscopy (EXANES/EXAFS) at the Stanford Synchrotron Radiation Laboratory

- Drs. David Shuh, Jerry Bucher, N.M. Edelstein, and Corwin Booth, LBNL
- Dr. Pat Allen, LLNL

Task: Neutron and High Energy X-Ray Scattering

- Drs. Marie-Louise Saboungi, Yaspal Badyal, and Dean Heaffner, The Division of Materials Science, Intense Pulsed Neutron Source, and The Advanced Photon Source, ANL

Task: Raman Spectroscopy

- Dr. Marcos Grimsditch, Division of Materials Science, ANL
- Dr. Andrea Mogus-Milankovic, Ruder Boskovic Institute, Croatia

Task: Electron Spin Resonance Studies

- Dr. David Griscom, Naval Research Laboratory

Task: Electrical properties (conductivity, loss, and dielectric constant)

- Dr. Andrea Mogus-Milankovic, Ruder Boskovic Institute, Croatia

*Collaboration Type:* Program interaction *Fiscal Year:* 1999
*Collaborator:* (See description)
*Collaborating Organization:* (See description)

*Description:* Drs. David Shuh, N. M. Edelstein, and Corwin Booth of the Actinide Chemistry Division provided experimental and theoretical support for x-ray absorption (EXAFS/XANES) studies conducted at the Stanford Synchrotron Radiation Laboratory (SSRL). Personnel from University of Missouri-Rolla visited both SSRL and LBNL to conduct experiments and to be trained in data analysis.
*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* Drs. David Shuh, N. M. Edelstein, & Corwin Booth
*Collaborating Organization:* LBNL

*Description:* Drs. Marie-Louise Saboungi and Yaspal Badyal provided experimental and theoretical support for neutron scattering studies conducted at the Intense Pulsed Neutron Source (IPNS). Dr. Dean Heaffner provided access to

the Advanced Photon Source (APS) for high energy x-ray scattering studies and Dr. Marcos Grimsditch provided experimental and theoretical support for Raman spectral studies. Personnel from UMR visited ANL to conduct experiments and to be trained in data analysis.

*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* Drs. Marie-Louise Saboungi, Yaspal Badyal, Dean Heaffner, & Marcos Grimsditch
*Collaborating Organization:* ANL

*Description:* We have recently developed an alternative waste form based on a new family of iron-phosphate glasses which appear to be well suited for many waste feeds, especially those which are incompatible with borosilicate glasses. This previous work at the University of Missouri-Rolla, done in collaboration with scientists from PNNL, Westinghouse Savannah River Laboratory, and LBNL, strongly suggests that iron phosphate glasses are a low cost and highly, effective alternative to borosilicate glasses for vitrifying selected nuclear wastes. Recently, Dr. Pat Allen of LLNL provided experimental and theoretical support for additional x-ray absorption (EXAFS/XANES) studies.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Dr. Pat Allen
*Collaborating Organization:* LLNL

*Description:* A thorough investigation of the structure and properties of iron-phosphate glasses and their wasteforms in the first part of this project has been made. Part of this work entailed the recruitment of top scientists at LBNL and ANL to study the specific structural aspects of these glasses. It is anticipated that this effort will continue in the future.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborating Organization:* LBNL and ANL

*Description:* We have recently developed an alternative waste form based on a new family of iron-phosphate glasses which appear to be well suited for many waste feeds, especially those which are incompatible with borosilicate glasses. This previous work at the University of Missouri-Rolla, done in collaboration with scientists from PNNL, Westinghouse Savannah River Laboratory, and LBNL, strongly suggests that iron phosphate glasses are a low cost and highly, effective alternative to borosilicate glasses for vitrifying selected nuclear wastes. Dr. Andrea Mogus-Milankovic of Ruder Boskovic Institute in Zagreb, Croatia, measured Raman/IR spectra and AC/DC conductivity of these iron phosphate glasses.

*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* Dr. Andrea Mogus-Milankovic
*Collaborating Organization:* Ruder Boskovic Institute, Zagreb, Croatia

*Description:* Two groups in Japan have become interested in our research on iron phosphate glasses. As part of a program on spent fuel recycling supported by the Japanese government, we were contacted by IHI (Ishikawajima-Harima Heavy Industries). IHI is coupled with IRI (Institute of Research and Innovation) to investigate alternative glasses

that could be used to vitrify the waste from fuel recycling and have made the decision to study iron phosphate glasses for that purpose. We gave them a briefing on our work in Tokyo in Nov 2000 and then a delegation (six persons) from both groups visited UMR in Feb 2001. We are working with them on an unofficial basis in reviewing their research plan, sharing our technical data, teaching them how to melt iron phosphate glasses, and reviewing their research results. We are pleased that there is interest in Japan in the iron phosphate glasses and that they see value in evaluating these glasses for their use.

*Collaboration Type:* Consulting *Fiscal Year:* 2001
*Collaborating Organization:* Ishikawajima-Harima Heavy Industries and Institute of Research and Innovation

*Description:* We have recently developed an alternative waste form based on a new family of iron-phosphate glasses which appear to be well suited for many waste feeds, especially those which are incompatible with borosilicate glasses. This previous work at the University of Missouri-Rolla, done in collaboration with scientists from PNNL, Westinghouse Savannah River Laboratory, and LBNL, strongly suggests that iron phosphate glasses are a low cost and highly, effective alternative to borosilicate glasses for vitrifying selected nuclear wastes. Dr. David Grisscom conducted Electron Spin Resonance spectral and Gas Evolved Mass Spectroscopy studies on iron phosphate glasses provided by University of Missouri-Rolla.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Dr. David Grisscom
*Collaborating Organization:* Naval Research Laboratory

## *Separations Chemistry*

### *Project: 54735*

*Title:* Development of Inorganic Ion Exchangers for Nuclear Waste Remediation
*PI:* Dr. Abraham Clearfield *Institution:* Texas A&M University at College Station

*Description:* This research is concerned with the development of highly selective inorganic ion exchangers for the removal of primarily Cs+ and Sr2+ from nuclear tank waste and from groundwater. In this study, we will probe the origins of selectivity through detailed structural studies, and the thermodynamics of the ion exchange processes. I am working with David Hobbs, whose group is testing our exchangers for removal of Sr, Pu, Np from SR tank waste.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* David Hobbs
*Collaborating Organization:* Savannah River

*Description:* This research is concerned with the development of highly selective inorganic ion exchangers for the removal of primarily Cs+ and Sr2+ from nuclear tank waste and from groundwater. In this study, we will probe

the origins of selectivity through detailed structural studies, and the thermodynamics of the ion exchange processes. The compounds to be synthesized may have cavity or tunnel structures, layer structures, or be amorphous gels. A key component to the development of this research has been the collaboration with a group of scientists at the Institute for Sorption and Problems of Endoecology (ISPE), in Kiev, Ukraine, where they have been concerned with remediation of the Chernobyl zone. Porous carbons treated with inorganic ion exchangers for soil and groundwater remediation have been devised, which sorb pesticides, Regicides, and heavy metals.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborating Organization:* Institute for Sorption and Problems of Endoecology (ISPE), Kiev, Ukraine

### *Project: 54996*

*Title:* Ionizing Radiation Induced Catalysis on Metal Oxide Particles
*PI:* Dr. Michael A. Henderson *Institution:* PNNL

*Description:* This project focuses on a novel approach for destroying organics found in high-level mixed waste prevalent at DOE sites. We have shown that ionizing radiation can be used to catalytically destroy organic chelating agents, such as EDTA, whose presence in high-level waste streams hinder the removal of radionucleii by ion exchange. Our studies have shown that gamma irradiation of titanium dioxide suspensions destroy the chelating ability of EDTA by decomposing it to smaller organic molecules. This has been demonstrated for both free EDTA in solution and for solutions of EDTA complexed to strontium. Present efforts are aimed at determining the mechanism by which EDTA is destroyed and the feasibility of using this process for treating high-level mixed waste.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* Abhaya K. Datye; Professor Miguel E. Castro
*Collaborating Organization:* University of New Mexico; University of Puerto Rico

### *Project: 73803 (Renewal of Project 55087)*

*Title:* Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation
*PI:* Dr. Bruce A. Moyer *Institution:* ORNL

*Description:* The PI has had an ESP project to develop processes for removal of fission products from high-level waste. The understanding gained from this EMSP task enabled the PI and his co-workers to solve a critcal problem in FY 1998. The understanding has also been useful in subsequent development through FY 2000. Although the carryover in the ESP budget is now exhausted, in the past quarter the PI was able to spend a few hours presenting results in a management briefing to Steve Richardson, DOE-ORO, and ORNL management. In addition, some ESP hours were spent presenting input to the National Academy of Sciences, which is reviewing the salt disposition situation at the SRS. This input consisted of answers to five questions regarding the status and

viability of the process for removing cesium from the high-level waste being stored at the SRS. The fundamental information obtained on cesium extraction equilibria was used indirectly in the presentation to Richardson and in the input to the National Academy. As a result, Richradson was excited about the possibility that the SRS is going to provide funds for further testing of the alkaline-side CSEX process. His reaction was to ask how he could facilitate ORNL being named lead laboratory for this testing. The NAS has not issued its report to the PI's knowledge, but it is likely based on its interim report issued in October that it will recommend that the SRS expend funds to accelerate the development of the process.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborating Organization:* EM-50 Efficient Separations and Processing (ESP) Crosscutting Program

*Description:* In order to supply the committee with data needed for its report to the USDOE Under Secretary, this project provided members of the team with information concerning the recent work, research, and performance accomplished in a presentation by P. V. Bonnesen in Nov. 1999. In Jan. and Mar. 2000, additional detailed information in the form of answers to written questions by committee members was provided as well. This information was incorporated into a WSRC report entitled "SRS High-Level Waste Salt Disposition Responses to NRC Questions of 1-11-00." In Aug. 2000, the committee issued its report based in part on this information, urging further testing of the CSEX process.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborating Organization:* National Academy of Sciences, National Research Council Committee on Salt Disposition at the SRS

*Description:* The Tanks Focus Area is managing the research and development program for the Salt Processing Project at the SRS. Three candidate cesuim removal technologies are being considered for down selection: Crystalline Siliconate Non-Elutable Ion Exchange (CST), Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipation (STTP). The research conducted under this EMSP project is directly applicable to the CSSX process. The principal investigator for this project is being funded by the Tanks Focus Area to bring their expertise and creativity to the development and selection process for this critical DOE project.

*Collaboration Type:* Consulting *Fiscal Year:* 2001
*Collaborating Organization:* Savannah River Salt Processing Project and Tanks Focus Area

*Description:* Due to the strong interaction with Westinghouse Savannah River Corp., Tanks Focus Area representatives were routinely kept informed. Members of the TFA continue to praise the progress made, encourage further work, and mediate interaction with the SRS. This past August, a large TTP was submitted from ORNL to the TFA to cover the demonstration and testing of the CSEX process for the SRS in FY 2001. This TTP has

been funded at the level of $1.8M. ANL will receive $0.85M, and the SRTC will receive $3.2M. The ORNL, ANL, and SRTC teams will work closely with each other.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborating Organization:* EM-50 Tanks Focus Area

*Description:* A combined effort at Oak Ridge, Pacific Northwest, and Argonne National Laboratories and the University of Tennessee is proposed to design, synthesize, and characterize the next generation of crown ethers for metal-ion separations applicable to USDOE's environmental needs. This research combines three inter-dependent projects dealing with 1) molecular mechanics and ligand design, 2) solvent-extraction properties, and 3) resin-immobilized crowns. Despite impressive developments in the chemistry of crown ethers, factors such as the need for polar environments and "forcing" conditions, weak efficiency, and dependence on matrix anions limits their potential in separations. Exploiting advances in molecular mechanics, this research seeks accelerated progress through ligand design and synthesis coupled with testing of predictions via structural, spectroscopic, and separation techniques. New crown compounds will be studied in solvent-extraction and polymer systems, emphasizing ion-exchange features. Selectivity principles governing the binding of such ions as Li+, Cs+, Sr2+, and Ra2+, all of which have been identified as contaminants at USDOE sites, will be investigated. The partner laboratories have world-recognized programs in the area of crown ethers, solvent extraction, and ion exchange. Their cooperation under this research represents an unusual and extremely effective combination of unique resources. As such, the US DOE Independent Project Evaluation Committee for cesium-removal technology selection for high-level tank waste at the SRS recently provided members of this team with information concerning the process and its performance.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborating Organization:* US DOE Independent Project Evaluation Committee for cesium-removal technology selection for high-level tank waste at the SRS

*Description:* Customer evaluation of the alkaline-side CSEX process as an alternative technology for replacement of the in-tank precipitation process was the main driving force behind this collaborative effort with Westinghouse Savannah River Corporation. A successful evaluation will result in further development, scale-up, demonstration, and pilot-scale testing. Ultimately, the main goal of this effort is implementation in a billion-dollar plant. At present, test results have been very positive, and the CSEX process appears competitive with current alternative technologies.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborating Organization:* Westinghouse Savannah River Corporation

# MIXED WASTE

## Actinide (Heavy Element) Chemistry

### Project: 54679

*Title:* Architectural Design Criteria for F-Block Metal Ion Sequestering Agents
*PI:* Dr. Benjamin P. Hay *Institution:* PNNL

*Description:* Critical tasks in the cleanup of U.S. Department of Energy (DOE) sites include processing radioactive wastes for disposal in long-term storage, remediation/restoration of environmental sites resulting from radioactive contamination, and decontamination/decommissioning of nuclear facilities. Because the radioactive components, most of which are metals, are typically present in very low concentrations, it is desirable to remove them from the bulk of the contaminated source and concentrate them to minimize the volume of radioactive material destined for permanent subsurface disposal and thus minimize disposal costs. Over the past 50 years, much research has focused on the discovery of selective ligands for f-block metal separations; both neutral and ionic ligands have been examined. Despite past success in the discovery of ligands that exhibit some degree of specificity for the f-block metal ions, the ability to further control binding affinity and selectivity remains a significant challenge. The objective of this project is to provide the means to optimize ligand architecture for f-block metal recognition. Criteria for accurately selecting target ligands would result in a much more effective use of resources, thereby reducing the time and cost associated with metal-specific ligand development. Collaborations for each associated task are as follows:

Task: Synthesis and characterization of modified calixarene host molecules.

- Professor D. Max Roundhill, Department of Chemistry, Texas Tech University

Task: Crystal structure determinations.

- Professor Robin D. Rogers, Department of Chemistry, The University of Alabama

Task: Synthesis of amides and diamides, through a subcontract with Associated Western Universities to support a Postdoctoral Fellow, Dr. Robert Gilbertson, in Dr. Hutchison's group.

- Professor James E. Hutchison, Department of Chemistry, University of Oregon

Task: Provide structure-function data on catecholates and hydroxypyridonates.

- Professor Kenneth N. Raymond, Department of Chemistry, University of California at Berkeley

Task: Provide structure-function data on pyridine N-oxides.

- Professor Robert T. Paine, Department of Chemistry, University of New Mexico

In addition to interactions with University faculty, the project has supported a variety of visitors at PNNL through Associated Western Universities subcontracts, including:

- Dr. Pier L. Zanonato (Visiting Faculty, University of Padova, Italy) - calorimetry
- Dr. Bruce K. McNamara (Postdoctoral Fellow) - calorimetry, spectroscopy, solvent extraction
- Dr. Omoshile Clement (Postdoctoral Fellow) - molecular mechanics
- Dr. Giovanni Sandrone (Postdoctoral Fellow) - quantum mechanics
- Dr. Rubicelia Vargas (Post Doctoral Fellow) - molecular mechanics and quantum mechanics
- Dr. Jorge Garza (Visiting Faculty, Metropolitan Autonomous University -Iztapalapa, Mexico) - quantum mechanics

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* (see description)
*Collaborating Organization:* (see description)

### *Project: 60370*

*Title:* Rational Design of Metal Ion Sequestering Agents
*PI:* Dr. Kenneth N. Raymond *Institution:* LBNL

*Description:* An enormous amount of radioactive and toxic chemical waste remains at over one hundred sites managed by the Department of Energy. Despite the investment of large sums major goals associated with the cleanup remain unmet. It is our thesis that economically practical accomplishments of these tasks will require technology not yet available. Basic studies of the sequestration of the relevant toxic metal ions is required in order to develop processes that will treat effluents sufficiently well to allow direct release into the environment, and minimize the production of secondary wastes. This research group has for many years led the development of new, metal-ion-selective sequestering agents. In what has been described as the first rational synthesis of such an agent, decontamination for Pu4+ have been developed. What is now proposed is the full thermodynamic and structural characterization of the metal-ligan systems that form the basis for rational metal-ion-specific ligand design. This will provide the basis for technologies targeted towards the separation and immobilization of hazardous metal ions. This project encompasses the synthesis of new materials, the physical characterization and evaluation of those materials, and the evaluation (and subsequent improvement) of these materials for interface to applied separation technologies.

Following these guidelines, Drs. Barbara Smith and Gordon Jarvinen of LANL recently synthesized and evaluated water-soluble chelating polymers, based on hydroxypyridinone and terephthalamide ligands attached to polyethyleneimine (PEI), as sequestering agents for uranyl, Pu, and Am.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Drs. Barbara Smith and Gordon Jarvinen
*Collaborating Organization:* LANL

*Description:* An enormous amount of radioactive and toxic chemical waste remains at over one hundred sites managed by the Department of Energy. Despite the investment of large sums major goals associated with the cleanup remain unmet. It is our thesis that economically practical accomplishments of these tasks will require technology not yet available. Basic studies of the sequestration of the relevant toxic metal ions is required in order to develop processes that will treat effluents sufficiently well to allow direct release into the environment, and minimize the production of secondary wastes. This research group has for many years led the development of new, metal-ion-selective sequestering agents. In what has been described as the first rational synthesis of such an agent, decontamination for Pu4+ have been developed. What is now proposed is the full thermodynamic and structural characterization of the metal-ligan systems that form the basis for rational metal-ion-specific ligand design. This will provide the basis for technologies targeted towards the separation and immobilization of hazardous metal ions. This project encompasses the synthesis of new materials, the physical characterization and evaluation of those materials, and the evaluation (and subsequent improvement) of these materials for interface to applied separation technologies.

Following these guidelines, Dr. Ben Hay of PNNL recently provided atomic coordinates from X-Ray crystal structures of actinide complexes of hydroxypyridinone, terephthalamide, and other ligands. This data is used in high level computational studies directed toward rational design of new actinide sequestering agents.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Dr. Ben Hay
*Collaborating Organization:* PNNL

*Description:* This project addresses the fundamental issues and requirements for developing hazardous metal ion separation technologies applicable to the treatment and disposal of radioactive waste. Our research encompasses the following areas: the design and synthesis of metal ion specific sequestering ligands, structural and thermodynamic investigations of these ligands and the complexes formed with targeted metal ions, and the development and incorporation of these ligands into applied separation technologies as highly effective materials for hazardous metal ion decontamination. This interaction has provided direct structural, thermodynamic and electrochemical studies of plutonium complexes.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Dr. Heino Nitsche
*Collaborating Organization:* LBNL

*Description:* An enormous amount of radioactive and toxic chemical waste remains at over one hundred sites managed by the Department of Energy. Despite the investment of large sums major goals associated with the cleanup remain unmet. It is our thesis that economically practical accomplishments of these tasks will require technology not yet available. Basic studies of the sequestration of the relevant toxic metal ions is required in order to develop processes that will treat effluents sufficiently well to

allow direct release into the environment, and minimize the production of secondary wastes. This research group has for many years led the development of new, metal-ion-selective sequestering agents. In what has been described as the first rational synthesis of such an agent, decontamination for Pu4+ have been developed. What is now proposed is the full thermodynamic and structural characterization of the metal-ligan systems that form the basis for rational metal-ion-specific ligand design. This will provide the basis for technologies targeted towards the separation and immobilization of hazardous metal ions. This project encompasses the synthesis of new materials, the physical characterization and evaluation of those materials, and the evaluation (and subsequent improvement) of these materials for interface to applied separation technologies.

Following these guidelines, Dr. Glen Fryxell of PNNL has recently synthesized ligands and developed a general synthetic methods to apply a broad range of coordinating groups as actinide sequestering agents in Self-Assembled Monolayers on Mesoporous Silica.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Dr. Glen Fryxell
*Collaborating Organization:* PNNL

## *Analytical Chemistry & Instrumentation*

### *Project: 54751*

*Title:* High Fluence Neutron Source for Nondestructive Characterization of Nuclear Waste
*PI:* Dr. Mark M. Pickrell
*Institution:* LANL

*Description:* The objective of the project is to research the basic plasma physics necessary to develop a high fluence neutron source based on the inertial electrostatically confined (IEC) plasma. An intense neutron source directly addresses the capability to characterize nuclear materials under difficult measurement conditions. Some of the applications for Environmental Management are the characterization of TRU wastes for WIPP, the measurements of residues prior to stabilization and disposal, the measurements of cemented or vitrified wastes, the measurement of spent nuclear fuel, and the measurement of high level wastes. Collaborations with the INEEL and the National Spent Nuclear Fuels Program to produce a neutron source for MDAS or other systems being developed by the INEEL.

Two commercial partners have applied for a license for the High Fluence Neutron Source, shown here in the laboratory. [see Project #54751]

*Collaboration Type:* Mission directed *Fiscal Year:* 1999
*Collaborator:* Jerry Cole
*Collaborating Organization:* INEEL

### *Project: 60070*

*Title:* The Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals
*PI:* Dr. George P. Miller *Institution:* Mississippi State University

*Description:* We have been asked to investigate the applicability of a suite of critical experiments planned to support the storage and transport of high-enriched, DOE/EM fuel. INEEL (INEEL) has significant quantities of highly enriched fresh and spent nuclear fuel in storage. INEEL has proposed to add to the data base of critical experiments relative to this application by having critical experiments performed in Russia. Prior to funding such experiments, INEEL has requested that ORNL use the S/U methodology and the SEN3 sequence to evaluate the neutronic similarity of the proposed experiments to the proposed application in transport and storage systems. Evaluations of these experiments have been completed and a draft report has been submitted to INEEL.
*Collaboration Type:* Joint interaction *Fiscal Year:* 2000
*Collaborator:* Blair Briggs
*Collaborating Organization:* INEEL

*Description:* We have been asked to study the relevance of current critical experiments to validation issues related to implementation of burnup credit in spent fuel safety analyses. Plans call for investigating the use of SEN3, a prototypic computational sequence for obtaining sensitivity and uncertainty (S/U) information for criticality safety applications, to evaluate adequacy of existing critical experiments and reactor critical configurations to validate codes for use in burnup credit in transport casks. SEN3 will be used to model the configurations and casks and the results used to evaluate similarity. Initial analysis of reactor critical configurations and proposed critical experiments have been completed and initial results used to provide NRC with guidance on top priority experiments for use in burnup credit.
*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* Dave Ebert
*Collaborating Organization:* United States Nuclear Regulatory Commision

### *Project: 73844 (Renewal of Project 60231)*

*Title:* Miniature Chemical Sensor Combining Molecular Recognition with Evanescent-Wave Cavity Ring-Down Spectroscopy
*PI:* Dr. Andrew C. R. Pipino *Institution:* National Institute of Standards & Technology - Maryland

*Description:* This project is developing a robust, rugged, portable, cost-effective sensor that has real-time chemical detection capabilities in gas, liquid, and semi-solid environments, and is therefore applicable in a variety of areas.

Research is currently focused on vapor phase sensing of trichloroethylene (TCE) and perchloroethylene (PCE). This sensor has the ability to be tailored to a variety of constituents based on the end users needs. As such, an on-going collaboration is occurring with the Nevada Field Office to address their need for uranium detection in soils and groundwater.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* John Jones and Bruce Crow
*Collaborating Organization:* DOE-NV

*Description:* This project is developing a robust, rugged, portable, cost-effective sensor that has real-time chemical detection capabilities in gas, liquid, and semi-solid environments, and is therefore applicable in a variety of areas. Research is currently focused on vapor phase sensing of trichloroethylene (TCE) and perchloroethylene (PCE). The researcher is working closely with the end user to develop a TCE sensor. Savannah River Technical Center has committed to field test this sensor upon its completion.

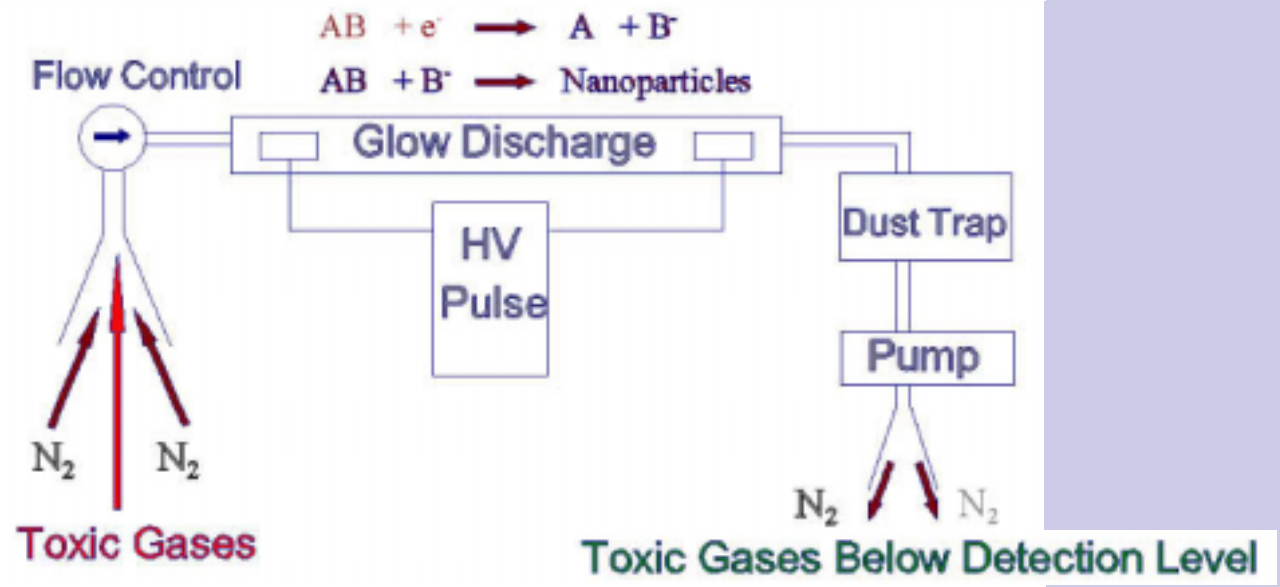
*Collaboration Type:* Mission directed *Fiscal Year:* 2001
*Collaborator:* Tim Smail
*Collaborating Organization:* Savannah River Technical Center

## *Engineering Science*

### *Project: 54973*

*Title:* A Novel Energy-Efficient Plasma Chemical Process for the Destruction of Volatile Toxic Compounds
*PI:* Dr. Lal A. (ORNL) Pinnaduwage *Institution:* ORNL

*Description:* Removal of low-concentrations (below several percent) of volatile toxic compounds (VTCs) from contaminated air streams is encountered at DOE waste sites in two instances: (i) Off-gases resulting from air-stripping of contaminated soil and water. (ii) Effluent from the incineration of highly-concentrated combustible hazardous wastes. The objective




Remediation of Toxic Gas Streams. [see Project #54973]

of our research program is to develop a novel plasma chemical process for the destruction of VTC's in low- concentration waste streams. Discussions have been initiated to determine applicability of this work to Paducah groundwater treatment problems and assess site interest. Mr. Richards expressed considerable interest in this approach and noted the timeframe of availability (assuming follow-on funding for development) was compatible with site plans.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborator:* Walt Richards
*Collaborating Organization:* Bechtel Jacobs Company, Paducah, KY

## *Inorganic Chemistry*

### *Project: 54506*

*Title:* Acid-Base Behavior in Hydrothermal Processing of Wastes
*PI:* Dr. Keith P. Johnston *Institution:* University of Texas at Austin

*Description:* A new technology, hydrothermal oxidation (also called supercritical water oxidation), is being developed to treat high level nuclear wastes. Nitrates are reduced to nitrogen; furthermore, phosphates, alumina sludge, and chromium are solubilized, and the sludge is reconstituted as fine oxide particles. A major obstacle to development of this technology has been a lack of scientific knowledge of chemistry in hydrothermal solution above 350 C, particularly acid-base behavior, and transport phenomena, which is needed to understand corrosion, metal-ion complexation, and salt precipitation and recovery. In an effort to understand these problems, collaborative work with LANL on experimentally treating tank waste with high temperatures is underway.

*Collaboration Type:* Joint interaction *Fiscal Year:* 1999
*Collaborator:* Steve Buelow
*Collaborating Organization:* LANL

### *Project: 54828*

*Title:* Processing of High Level Waste: Spectroscopic Characterization of Redox Reactions in Supercritical Water
*PI:* Dr. Charles A. Arrington, Jr. *Institution:* Furman University

*Description:* Current collaborative research efforts with LANL on the oxidative dissolution of chromium compounds found in Hanford tank waste sludge include focusing on the destructions of complexants and oxidation of chromium and technetium by hydrothermal processing in near critical or supercritical aqueous solutions. Samples of chromium oxides and hydroxides with varying degrees of hydration are being characterized using Raman, FTIR, and XPS spectroscopic techniques. Kinetics of oxidation reactions at subcritical and supercritical temperatures are being followed by Raman spectroscopy using a high temperature stainless steel cell with diamond windows. In these reactions both hydrogen peroxide and nitrate anions are used as the oxidizing species with Cr(III) compounds and organic compounds as reducing agents. The work proposed by these LANL staff scientists is directed towards the destruction of complexants

and oxidation of chromium and technetium by hydrothermal processing in near critical or supercritical aqueous solutions. Experimental work was conducted at LANL during the summers and at Furman during the academic years.

*Collaboration Type:* Mission directed *Fiscal Year:* 1999
*Collaborator:* Steven Buelow and Jeanne Robinson
*Collaborating Organization:* LANL

### *Project: 59934*

*Title:* Hazardous Gas Production by Alpha Particles in Solid Organic Transuranic Waste Matrices
*PI:* Dr. Jay A. LaVerne *Institution:* University of Notre Dame

*Description:* Hazardous gas production by the self-radiolysis of solid organic matrices, such as polymers and resins, containing radioactive material is a serious problem for waste management. Hydrogen is the most common hazardous gaseous product, although methane and ethane are possible, depending on the particular material. The yield of these products can be an order of magnitude different between alpha particles and gamma rays. Studies are in progress to estimate hazardous gas production in various solid matrices with different radiation. Fundamental knowledge on radiation chemical processes is being transferred to interested researchers at LANL.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborating Organization:* Los Almos National Laboratory

## *Separations Chemistry*

### *Project: 55103*

*Title:* Utilization of Kinetic Isotope Effects for the Concentration of Tritium
*PI:* Dr. Gilbert M. Brown *Institution:* ORNL

*Description:* The objective of our work is to develop an electrochemically-based, cyclic process which can be used to remove tritium from contaminated water. We are developing methods for concentrating tritium from water based on large primary kinetic isotope effects in catalytic redox processes. H-T discrimination occurs in an oxidation step involving a transition metal oxidant and small organic compounds containing oxidizable C-H or C-T bonds. Tritium is incorporated in the organic compound by an electrochemical reduction process in the presence of tritium contaminated water, but the protio-derivative is kinetically favored in the oxidation half-reaction. As a result of a cyclic oxidation-reduction process, tritium is enriched in the organic compound. The organic compound is chosen so that it does not readily exchange the tritium with groundwater.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* C.H. Ho, Douglas J. Lemme, Leon Maya, and Frederick V. Sloop, Jr.; Poonam M. Narula and Thomas J. Meyer
*Collaborating Organization:* ORNL; University of North Carolina at Chapel Hill

# NUCLEAR MATERIALS

## Engineering Science

### Project: 60077

*Title:* Development of Nuclear Analysis Capabilities for DOE Waste Management Activities

*PI:* Dr. Cecil V. Parks *Institution:* ORNL

*Description:* Performance of an analysis of proposed experiments and prototypic spent fuel shipping and storage applications for the INEEL (INEEL). This analysis used the sensitivity analysis techniques developed under the EMSP project, in conjunction with other newly developed sensitivity and uncertainty analysis techniques, to determine whether a proposed set of critical experiments met the needs of INEEL for the validation of nuclear safety analysis software used in the design of shipping and storage applications for DOE-owned spent nuclear fuel. A preliminary report has been submitted to INEEL, and follow-up work is continuing.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2000

*Collaborating Organization:* INEEL

*Description:* The objective of this project is to develop and demonstrate prototypical analysis capabilities that can be used by nuclear safety analysis practitioners to: (1) provide a more thorough understanding of the underlying physics phenomena that can lead to improved reliability and defensibility of safety evaluations; and (2) optimize operations related to the handling, storage, transportation, and disposal of fissile material and DOE spent fuel. To address these problems, this project will investigate the implementation of sensitivity and uncertainty methods within existing Monte Carlo codes used for criticality safety analyses, as well as within a new deterministic code that allows for specification of arbitrary grids to accurately model geometric details required in a criticality safety analysis. A study of the application of sensitivity and uncertainty methodology to relevant EM problems of current interest was conducted. With the help of Michaele Brady Raap at Hanford and Todd Taylor at INEEL, ORNL researchers reviewed applications related to the tank farms and disposal of spent nuclear fuel to assess the potential changes in safety margin that might be achieved using the sensitivity and uncertainty methodology.

*Collaboration Type:* Program interaction *Fiscal Year:* 1999

*Collaborator:* Michaele Brady Rapp (Hanford) and Todd Taylor (INEEL)

*Collaborating Organization:* DOE Nuclear Criticality Safety Program

*Description:* A study of the relevance of current critical experiments to validation issues related to implementation of burnup credit in spent fuel safety analyses. Plans originally called for the investigating of the use of SEN3 to evaluate adequacy of existing critical configurations to validate codes for use in burnup credit in transport casks. SEN3 will be used to model the configurations and casks and the results used to evaluate similarity.

*Collaboration Type:* Consulting *Fiscal Year:* 2000

*Collaborator:* Dave Ebert

*Collaborating Organization:* United States Nuclear Regulatory Commission

*Description:* INEEL has significant quantities of highly enriched fresh and spent nuclear fuel in storage. INEEL has proposed to add to the database of critical experiments relative to this application by having critical experiments performed in Russia. Prior to funding such experiments, INEEL has requested that ORNL use the S/U methodology and the SEN3 sequence to evaluate the neutronic similarity of the proposed experiments to the proposed application in transport and storage systems.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Blair Briggs
*Collaborating Organization:* INEEL

### *Materials Science*

#### *Project: 55094*

*Title:* Chemical and Ceramic Methods Toward Safe Storage of Actinides Using Monazite
*PI:* Dr. P. E. D. Morgan *Institution:* Rockwell International Corporation

*Description:* To investigate the role of radiation damage in altering potential media for the disposition of Pu and other actinides, heavy particle radiation damage experiments were performed, and the damage effects were characterized using TEM, electron diffraction, and other techniques. The experimental results formed the basis for a new model that can be used to predict wasteform stability in the case of Pu storage.

*Collaboration Type:* Program interaction *Fiscal Year:* 1997
*Collaborator:* Prof. R. C. Ewing
*Collaborating Organization:* Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI

*Description:* The interaction between electron beams and the rare-earth orthophosphates as manifested by cathodoluminescence were investigated. New information was obtained that can be applied to the analysis of complex ceramics that contain monazite as a constituent phase.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Dr. John M. Hanchar
*Collaborating Organization:* University of Notre Dame, Department of Civil Engineering and Geological Sciences, Notre Dame, IN. (BES project)

*Description:* To investigate the role of radiation damage in perovskite and pyrochlore phases that are constituents of titanate (SYNROC)-type ceramics for Pu disposal, techniques for the growth of pyrochlore single crystals were developed, and TEM and RBS studies of radiation effects in perovskites and pyrochlores were carried out. New insight into the radiation resistance of pyrochlore and perovskite phases has been obtained.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Dr. W. J. Weber
*Collaborating Organization:* Battelle Pacific Northwest Laboratory, Richland, WA. (EMSP Project 54672)

### Project: 60118

*Title:* Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms
*PI:* Dr. Mark A. Williamson *Institution:* ANL

*Description:* The end of the Cold War raised the need for the technical community to be concerned with the disposition of excess nuclear weapon material. The plutonium will either be converted into mixed-oxide fuel for use in nuclear reactors or immobilized in glass or ceramic waste forms and placed in a repository. The stability and behavior of plutonium in the ceramic materials as well as the phase behavior and stability of the ceramic material in the environment is not well established. The purpose of this project is to determine the thermodynamic data essential to developing an understanding of the chemistry and phase equilibria of the waste form materials proposed as immobilization matrices. Collaboration with DOE-MD program for Dispositioning of Plutonium by Immobilization.

*Collaboration Type:* Program interaction *Fiscal Year:* 1999
*Collaborating Organization:* DOE-MD

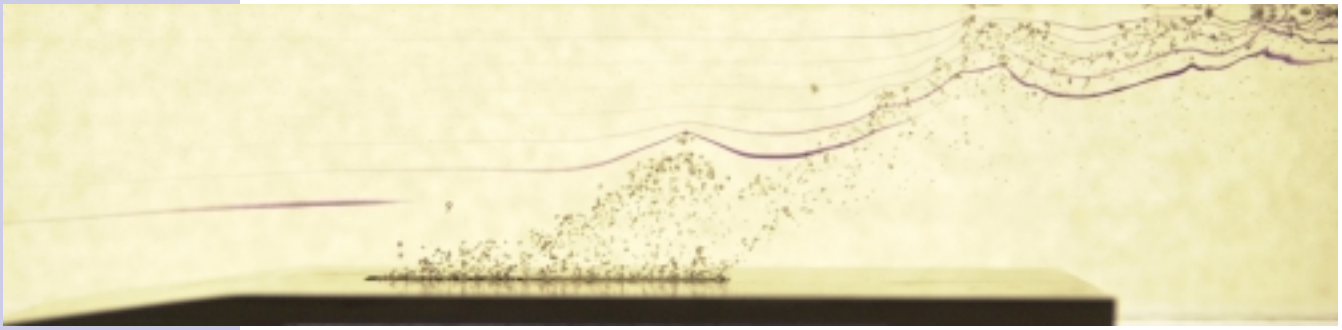
## SPENT NUCLEAR FUEL

### Engineering Science

### Project: 60144

*Title:* Flow Visualization of Forced and Natural Convection in Internal Cavities
*PI:* Dr. John C. Crepeau *Institution:* University of Idaho

*Description:* The INEEL has developed a half-scale experiment to measure fluid dynamic processes in an idealized SNF canister by fabricating a quartz model for use in INEEL's unique large Matched-Index-of Refraction flow system. Currently, two-component laser Doppler velocimetry is used to measure velocity and turbulence components. The present experiment is aimed at examining basic, generic flow processes occurring. Measurements to date emphasize the semi-confined impigning jet and recirculating flow in the region between the perforated basket support plate and the bottom of the canister in a hypothesized approach for drying and passivation. These data should be valuable for assessing and benchmarking



A fluid containing hexanoic acid reacts with sodium metal embedded in an aluminum plate to produce hydrogen bubbles. The dye illustrates the disturbances in the flow caused by the bubbles. This reaction simulates a passivation reaction during treatment of corroded spent nuclear fuels. [see Project #60144]

computer codes purported to predict flow patterns in SNF canisters during these operations. The status and plans of this project were presented to the National and INEEL SNF Programs at the 2nd EM Science Workshop and further discussions were subsequently held with the National SNF Program staff. An earlier summary was presented to the SNF technical community at the ANS Topical Meeting in Charleston, SC.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborating Organization:* National and INEEL SNF Programs

*Description:* The goal of this program is to develop innovative flow visualization methods and predictive techniques for energy, mass and momentum transfer in the presence of chemical reactions in the drying and passivation of spent nuclear fuel (SNF) elements. Efforts on this project are coordinated with the National Spent Nuclear Fuel programs. Their staff have provided guidance on the wide range of SNF canister configurations and fuel elements in use; from this information this EMSP project has developed the descriptions of generic flow processes of concern and, thereby, designed the experiments conducted. The SNF staffs have provided understanding of needs for fundamental studies and have reviewed project results and plans for our fundamental studies.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborating Organization:* National Spent Nuclear Fuel programs

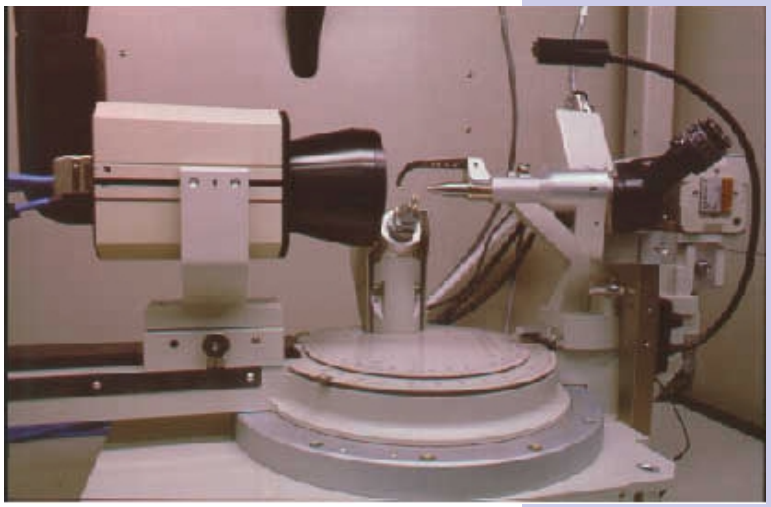
## Geochemistry

### Project: 73691 (Renewal of Project 59960)

*Title:* Renewal of Direct Investigations of the Immobilization of Radionuclides in the Alteration Products of Spent Nuclear Fuel

*PI:* Dr. Peter C. Burns *Institution:* University of Notre Dame

*Description:* In an oxidizing environment, such as the proposed repository at Yucca Mountain (YM), rapid alteration rates are expected for spent nuclear fuel. Laboratory-scale simulations demonstrate that the dominant alteration products under YM repository conditions will be uranyl phases. There is an inadequate database to relate the effects of alteration products to the release of radionuclides, although this information is essential for providing realistic radionuclide-release estimates. It is likely that



The CCD-based X-ray diffraction system used to determine the structures of many uranyl phases. [see Project #73691, renewal of #59960]

An SEM image of a new uranyl silicate phase found growing on actinide-bearing borosilicate wasteglass (S51) from Savanna River. The glass was placed in 100% humidity at 200?C for 60 days. This phase is new to science. The crystal structure was determined using X-ray diffraction, and obtained chemical analysis with an electron probe. This phase is potentially a very important sink for actinides where waste forms are altered under repository conditions. [see Project #73691, renewal of #59960]

many radionuclides contained in spent fuel will be incorporated into alteration products with a potentially profound impact on the future mobility of radionuclides in the repository. Our objective is to characterize the incorporation of radionuclides into U(VI) alteration products by synthesizing uranyl phases doped with radionuclides, appropriate surrogate elements, or non-radioactive isotopes, followed by detailed phase characterization by diffraction and spectroscopic techniques. This research will permit a more realistic estimate of the release rates of radionuclides from the repository's near-field environment.

In collaboration with Rudolph Olson of ANL, we solved the crystal structure of a novel uranyl silicate formed during the corrosion of an actinide-bearing waste glass. The structure contains sheets of eight- and four-membered silicate tetrahedral rings, linked together by uranyl square bipyramids. Channels within the uranyl silicate framework are occupied by low valence cations including K and Na, as well as water molecules. We expect this phase to form under YM repository conditions.

*Collaboration Type:* Program interaction
*Fiscal Year:* 1999
*Collaborator:* Rudolph Olson
*Collaborating Organization:* ANL

*Description:* The National Spent Nuclear Fuels Program (NSNFP) is interested in this research concerning the mobility of the radionuclides in Spent Nuclear Fuels (SNF) for their work on the repository at Yucca Mountain. Dr. Burns is collaborating with ANL-E, where they are performing drip tests in a hot cell on commercial SNF. Ms. Davis has a work package funded by the NSNFP which funds ANL-E to perform similar release rate testing on DOE SNF. She is interested in having Dr. Burns perform an analysis on DOE SNF, similar to what he has done on commercial SNF. Dr. Paul Lessing is investigating the incorporation of Gadolinium as a neutron absorber into the DOE SNF packages which will be sent to Yucca Mountain. He would be interested in having Dr. Burns investigate the mobility of Gd in SNF packages.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborator:* Colleen Shelton-Davis
*Collaborating Organization:* National Spent Nuclear Fuels Program

### *Project: 73751 (Renewal of Project 59849)*

*Title:* Corrosion of Spent Nuclear Fuel: The Long Term Assessment
*PI:* Dr. Rodney C. Ewing *Institution:* University of Michigan

*Description:* In the area of spent nuclear fuel corrosion, we maintain an active program of collaborations with the following individuals:

Dr. Peter Burns, Notre Dame University
- structural studies and refinements of uranium minerals.

Dr. Jordi Bruno, QuantiSci, Barcelona, Spain
- leaching studies of uranium minerals; solution chemistry of actinides.
- studies on the corrosion of UO2.

Dr. Ignasi Casas, Department of Chemistry, UPC, Barcelona, Spain
- leaching studies of uranium minerals.
- studies on the corrosion of UO2.

Dr. Fanrong Chen, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, P.R. China
- geochemical modeling of uranium-phase dissolution.

Professor Sue Clark, Department of Chemistry Washington State University
- structure-based models of solubility.
- on the incorporation of radionuclides into U(6+) compounds.

Dr. Mostafa Fayek, Center of Isotope Geochemistry, ORNL
- isotopic studies of uranium deposits.

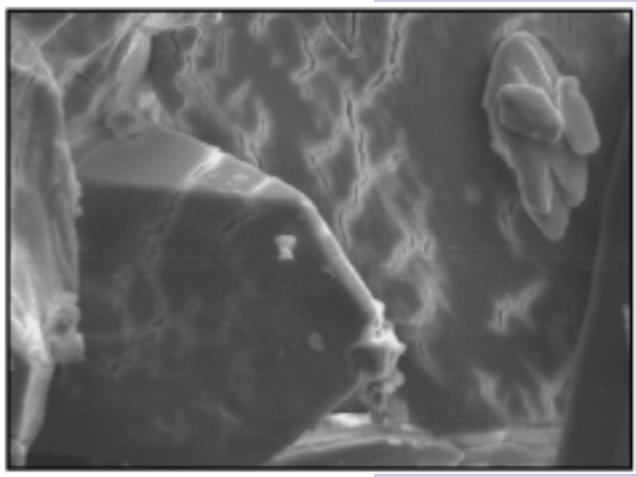
Professor Frank Hawthorne, Department of Geological Sciences, University of Manitoba
- crystal structure refinements of uranium minerals.

Professor Hiroshi Hidaka, Department of Earth And Planetary Systems Science, Hiroshima University
- SIMS analysis of uranium-bearing phases.

Professor Janusz Janeczek, Faculty of Earth Sciences, University of Silesia
- mineralogy and geochemistry of the Oklo reactors.

Professor Takashi Murakami, Mineralogical Institute, Tokyo University
- studies of uranium phases by FEG-TEM and x-ray diffraction analysis.

Dr. Juan de Pablo, Department of Chemical Engineering UPC, Barcelona, Spain
- leaching studies of uranium minerals.



SEM-image of a uranyl sulfate hydrate precipitate on johanneite from the Oklo open pit. [see Project #73751, renewal of #59849]

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* (see description)
*Collaborating Organization:* (see description)

*Description:* The UO2 in spent nuclear fuel is not stable under oxidizing conditions. Under oxic conditions, the U(IV) has a strong tendency to exist as U(VI) in the uranyl molecule, UO22+. The uranyl ions react with a wide variety of inorganic and organic anions to form complexes which are often highly soluble. The result is rather rapid dissolution of UO2 and the formation of a wide variety of uranyl oxide hydrates, uranyl silicates and uranyl phosphates. The reaction rates for this transformation are rapid, essentially instantaneous on geologic time scales. Over the long term, and depending on the extent to which these phases can incorporate fission products and actinides, these alteration phases become the near-field source term. Based on those guidelines, a survey of the role of colloids in spent fuel corrosion and radionuclide mobility was recently conducted for the National Spent Fuel Program at the INEEL.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborating Organization:* INEEL

*Description:* Dr Rodney C. Ewing, PI, has been asked to paricipate in the TRW Environmental Division review of the total system performance of the Yucca Mountain Repository and the Nuclear Waste Technology Review Board review of the TSPA of the Yucca Mountain Repository.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborating Organization:* TRW Environmental Division

## SUBSURFACE CONTAMINATION

### Actinide (Heavy Element) Chemistry

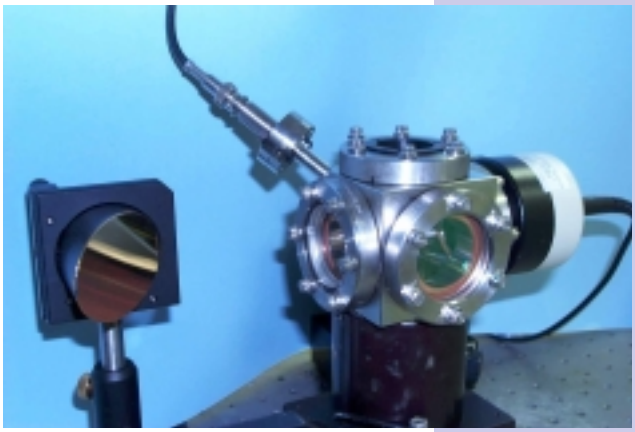
#### Project: 70050

*Title:* Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone
*PI:* Dr. S. Michael Angel *Institution:* University of South Carolina

*Description:* DOE requires improved technologies for characterization and monitoring for site clean-up and waste processing applications. Especially needed are field deployable methods and devices for real-time monitoring to reduce dependency on laboratory analyses that are costly and time consuming. Improved sensing capabilities are needed for on-site analyses to provide real-time analytical capabilities for screening level and/or decision-quality data. Matrices of interest to the DOE are soils (or other solids), slurries, and aqueous and non-aqueous solutions. In-situ methods have been demonstrated for identifying high concentrations of organic liquids (e.g., Raman spectroscopy) and low concentrations of a few types of organic molecules (e.g., UV fluorescence and DUVAS), as well as a few selected organic molecules (e.g., sensors) at low concentrations. However, currently there is no method for measuring low levels of organic vapors of the type that would be indicative of subsurface contamination in the vadose zone. The proposed research focuses specifically on a method, resonance-enhanced multi-photon ionization—REMPI, for measuring organic solvents in a soil matrix by detecting organic vapors in the vicinity of a NAPL. We propose using this technique in

combination with Raman spectroscopy thus allowing organic contaminants to be measured and identified over a very wide range of concentrations. Our proposed REMPI studies are different from current approaches in that we will use a visible laser for excitation rather than a UV laser, as is used by other groups, to reduce the cost and complexity of the instrumentation, and make the system more robust and reliable. Furthermore, visible wavelengths are more compatible with existing fiber-optic probes and will make it easier to make field measurements using long fiber cables.

A highly multidisciplinary collaborative group of scientists has been assembled for this project. Angel (analytical chemist with experience with sensors and probe designs), Gribb (civil engineer with expertise in hydraulic measurements, cone penetrometer measurements and soil column design), Colston, Gold, and Brown (expertise in OPO laser measurements, cone penetrometer instrumentation, and subsurface measurements using fiber optics). Furthermore, experts in cone penetrometer experiments will help in the field studies.



LLNL VOC test chamber with achromatic free space focusing. [see Project #70050]

*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* Bill Colston, David M. Gold, and Steve Brown
*Collaborating Organization:* LLNL

*Description:* An in-situ field test of a prototype REMPI detection instrument is in the planning stages. Laboratory results indicate ppb detection levels of some VOC's (toluene, benzene, etc.) even within complex mixtures with a simple probe which is compact enough for integration into a cone penetrometer and rugged enough for field testing. The collaboration will utilize experts in cone penetrometry field tests at the SRS (SRS), the technical and fabrication abilities of LLNL, and the analytical chemistry measurements of USC.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Joseph Rossabbi
*Collaborating Organization:* SRS

### *Project: 70132 (Renewal of Project 54683)*

*Title:* Speciation, Mobility and Fate of Actinides in the Groundwater at the Hanford Site
*PI:* Dr. Ken O. Buesseler *Institution:* Woods Hole Oceanographic Institute

*Description:* High sensitivity thermal ionization mass spectrometry (TIMS) is used to detect the Pu isotopes in all size and redox fractions, thus providing

information not only on Pu concentrations but on the Pu source, which can strongly influence Pu speciation and mobility. The combination of these state-of-the-art procedures and the demonstrated care taken to process these samples ensures that the data represent the original in-situ speciation. The results of such a careful basic research program would: i) provide the basis for accurate modeling and prediction of actinide transport; ii) allow for remediation strategies to be planned that might use in-situ manipulations of geochemical variables to enhance (for extraction) or retard (for immobilization) Pu mobility in the vadose/groundwater zone, and iii) identify specific Pu sources and the extent of far field, or long-term migration of actinides in groundwaters. This new knowledge is essential to ensure continued public and worker safety at the DOE sites and the efficient management of cleanup and containment strategies. Based on this research, our project is collaborating with PNNL utilizing the TIMS facility to study Pu ratios for transport rates. Field sampling is also being done at SRS F basin and Handford 100 K Area to support plume definition and predictive modeling efforts.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborating Organization:* PNNL

***Project: 70176***

*Title:* Transuranic Interfacial Reaction Studies on Manganese Oxide Hydroxide Mineral Surfaces

*PI:* Dr. Heino Nitsche *Institution:* LBNL

*Description:* Several DOE sites have been contaminated by transuranic radionuclides (TRU). Manganese oxide/hydroxide minerals, present as minor phases in the vadose zone, can preferentially sequester TRU over iron oxides and other minerals present in much larger quantities. In order to understand the interactions between TRU and manganese oxyhydroxide minerals, we are investigating interfacial reactions between plutonium and manganese based minerals relevant to contaminant transport in the vadose zone. We are currently determining the parameters governing the sorption of aqueous plutonium(VI) ions on well-characterized mineral surfaces as a function of pH, actinide concentration and ionic strength. These investigations will be extended to plutonium(V) and plutonium(IV) as well. In addition to sorption measurements, we are also using x-ray absorption fine structure (XAFS) spectroscopy to determine the local structure and oxidation states of the sorbed plutonium ions.

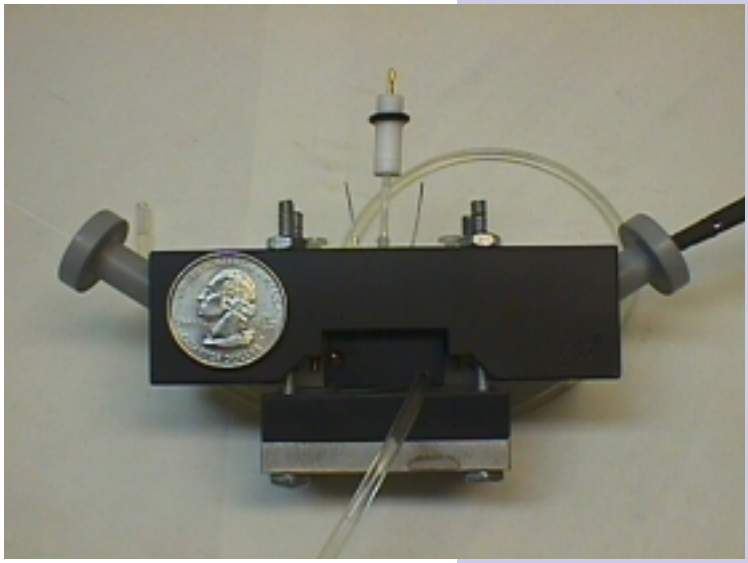
*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* R. J. Serne
*Collaborating Organization:* PNNL

## *Analytical Chemistry & Instrumentation*

### *Project: 70010 (Renewal of Project 54674)*

*Title:* Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone
*PI:* Dr. William R. Heineman *Institution:* University of Cincinnati

*Description:* A proposed new sensor concept combines the elements of electrochemistry, spectroscopy, and selective partitioning into a single device that provides three levels of selectivity. This type of sensor has many potential applications at DOE sites. As an example, the enhanced specificity embodied in this new sensor design is well-suited to the analytical problem posed by the addition of ferrocyanide to radioactive tank wastes at the DOE-Hanford Site. A demonstration of a sensor package (mircocell and instrumentation) was performed on the waste tank sample.



Prototype sensor can accommodate a sample volume of 800 mL. Working electrode consists of an indium tin oxide slide coated with a charge selective film; the blue LED provides a simple light source. [see Project #70010, renewal of #54674]

*Collaboration Type:* Program interaction
*Fiscal Year:* 2000
*Collaborator:* Dr. Heineman - University of Cincinnati
*Collaborating Organization:* Hanford Site

### *Project: 70179*

*Title:* Radionuclide Sensors for Water Monitoring
*PI:* Dr. Jay W. Grate *Institution:* PNNL

*Description:* Our research program is directed toward developing novel sensor concepts and materials for sensitive and selective determination of beta- and alpha-emitting radionuclide contaminants in water. In order to meet the requirements for isotope specific detection at ultra-low regulatory levels the proposed sensors are based on radiometric detection. In order to address the fundamental challenge of short ranges of beta and alpha particles in water, our overall approach is based on localization of preconcentration/separation chemistries directly on or within the active area of a radioactivity detector, using automated microfluidics for sample manipulation and sensor regeneration or renewal. Radionuclides of primary interest for DOE needs are Sr-90, Tc-99, and actinides. Jim Roane a Ph.D. student from Clemson who is involved in work on this EMSP program, worked with Drs. John Leyba and Raymond Sigg at the SRS evaluating the TEVA and ABEC extractive scintillator materials for potential application of on-line process monitoring for Tc.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2000
*Collaborating Organization:* SRS

*Description:* We have established collaboration with the University of Arkansas at Little Rock (Professor Malay Mazumder, Department of Applied Sciences) on the synthesis and production of dual functionality scintillator/ sorbent materials for radionuclide sensing. Dr. Mazumder will explore electrostatic microencapsulation methods to produce materials with required properties.

*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* Dr. Malay Mazumder
*Collaborating Organization:* University of Arkansas at Little Rock

## *Biogeochemistry*

### *Project: 55388*

*Title:* Stable Isotopic Investigations of In Situ Bioremediation of Chlorinated Organic Solvents
*PI:* Dr. Neil C. Sturchio *Institution:* ANL

*Description:* The purpose of this project was to investigate the potential applications of stable isotope ratio measurements in characterization of the source terms, the transport, and the fate of chlorinated solvents in groundwater aquifers. The approach to this research was threefold: to develop methods for the sampling and isotopic analysis of chlorinated solvents in groundwaters; to perform laboratory experiments to measure equilibrium and kinetic isotope effects associated with biological and physical transformation processes of chlorinated solvents; and to perform field investigations at well-characterized, contaminated aquifer sites to demonstrate the applicability of the isotopic approach in real-world situations. To further these means the following collaborations were established:

- Mr. Jay Clausen (Lockheed-Martin Energy Systems, Inc., Kevil, KY (now at Ogden Energy and Environmental Systems, Inc., Westport, MA), on application of chlorine isotope ratio measurements in an investigation of natural attenuation of trichloroethene at the Paducah Gaseous Diffusion Plant.

- Mr. Greg Smith, ENSR, Inc. (now at Radian International), on application of carbon and chlorine isotopic measurements to solvent cleanup activities at a number of industrial sites.

- Dr. Chris Reddy, Woods Hole Oceanographic Institute, Woods Hole, MA, on application of chlorine isotope measurements to environmental studies of semivolatile chlorinated organics (e.g., PCBs and pesticides).

*Collaboration Type:* Mission directed *Fiscal Year:* 2000
*Collaborator:* (see description)
*Collaborating Organization:* (see description)

### Project: 70063 (Renewal of Project 54666)

*Title:* Biodegradation of Chlorinated Solvents: Reactions Near DNAPL and Enzyme Function

*PI:* Dr. Perry L. McCarty

*Institution:* Stanford University

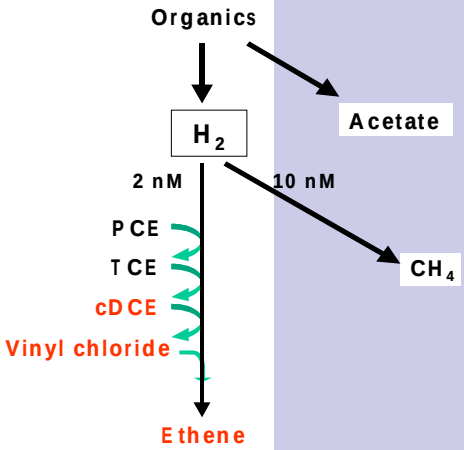
*Description:* The effects of radiation from the decay of radionuclides in nuclear waste and other nuclear materials may potentially impact the long-term performance and stability of nuclear waste forms and stabilized nuclear materials. Using experimental and computer simulation approaches, this project endeavors to develop the underpinning science and models necessary to assess the effects of radiation on the performance of glasses and ceramics designed for the immobilization of high-level tank waste and stabilized nuclear materials. Collaborations with PNNL and LANL have been developed to help further these objectives.

*Collaboration Type:* Program interaction

*Fiscal Year:* 2000

*Collaborator:* N.J. Hess, B.D. Begg, L.R. Corrales, H.L. Heinisch, and R.E. Williford; S.D. Conradson

*Collaborating Organization:* PNNL; LANL




PCE (or TCE) is stepwise reductively dehalogenated to the less chlorinated ethenes cDCE and VC. Concentration values indicate the hydrogen threshold concentration below which a pathway (dehalogenation or methanogenesis) usually does not operate. [see Project #70063, renewal of #54666]

### Project: 70165

*Title:* Integrated Field, Laboratory, and Modeling Studies to Determine the Effects of Linked Microbial and Physical Spatial Heterogeneity on Engineered Vadose Zone Bioremediation

*PI:* Dr. Fred J. Brockman *Institution:* PNNL

*Description:* In situ bioremediation of contaminants can offer advantages in cost, speed, public acceptance, and final cleanup levels achieved relative to physical removal methods. However, the lack of knowledge on how physical and hydrologic features of the vadose zone control the spatial distribution of microbial biotransformation activity and the potential for microorganisms to colonize this region raises questions about the feasibility of deep vadose zone bioremediation, and causes very large uncertainties in the accuracy of current model predictions. Because of the PI's understanding biological processes and bioremediation in the vadose zone, he has been asked by INEEL to write the biological transformation processes portion of the Vadose Zone Complex Wide Science Needs and Capabilities document.

*Collaboration Type:* Consulting *Fiscal Year:* 2000

*Collaborating Organization:* INEEL

### *Project: 73784 (Renewal of Project 55267)*

*Title:* Microbially Mediated Immobiliuzation of Contaminants Through In Situ Biostimulation: Scale up of EMSP project 55267

*PI:* Dr. Philip M. Jardine *Institution:* ORNL

Experiments by an EMSP project are designed to help determine optimum operating conditions for hydrothermal oxidation of aqueous mixed wastes. In this photo, scientists load uranium (VI) oxide samples into a rocking autoclave for solubility measurements at high temperatures. [see Project #73784, renewal of #55267]

*Description:* The purpose of this research is to provide an improved understanding and predictive capability of the mechanisms that allow metal-reducing bacteria to be effective in the bioremediation of subsurface environments contaminated with toxic metals and radionuclides. The study is motivated by the likelihood that subsurface microbial activity can effectively alter the redox state of toxic metals and radionuclides so that they are immobilized for long time periods. The overall goal of this project is to use basic research to develop a cost effective remediation strategy that employs in situ contaminant immobilization. Specifically, we will develop active biowall technologies to contain priority EM contaminant plumes in groundwater. Interaction with several other EMSP projects with regard to technology transfer, data sharing, and collaboration on experimental designs.

*Collaboration Type:* Program interaction

*Fiscal Year:* 2000

*Collaborator:* Dr. Eric Roden (EMSP Project 55164) and Dr. Lenly Weathers (EMSP Project 55071)

*Collaborating Organization:* University of Alabama and Tennessee Technological University

## *Engineering Science*

### *Project: 70088*

*Title:* Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone

*PI:* Dr. Baolin Deng *Institution:* New Mexico Institute of Mining & Technology

*Description:* Immobilization of toxic and radioactive metals (e. g., Cr, Tc, U) in the vadose zone by in situ gaseous reduction (ISGR) using hydrogen sulfide (H2S) is a promising technology being developed by the U. S. Department of Energy (DOE) for soil remediation. Earlier laboratory studies at the PNNL (PNNL) have shown that Cr(VI) in a number of soil samples can be effectively immobilized by treatment with diluted H2S. A field test has also been completed which resulted in 70% immobilization of Cr(VI). The objective of this collaborative project between PNNL and New Mexico Tech is to seek basic scientific understanding concerning

the kinetics and mechanisms of interactions among H2S, the metal contaminants, and soil components.

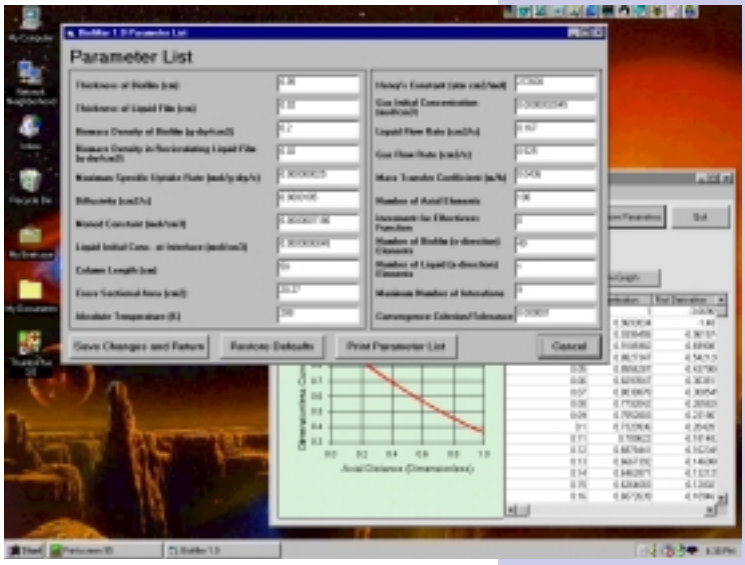
*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborating Organization:* PNNL

### *Project: 73793 (Renewal of Project 55013)*

*Title:* Biofiltration of Volatile Pollutants: Solubility Effects
*PI:* Dr. Brian H. Davison *Institution:* ORNL

*Description:* This work seeks to produce industrial and EM-relevant scientific information for successful biofiltration operation with a continued emphasis on in situ, discussion of current TCE treatment by air stripping, and biological degradation using methane at SRS. A discussion regarding how better data and modeling tools could help select remediation approaches was held. The difficulty of bringing fundamental research to deployment, end-user, and focus group needs has also been examined. SRS has indicated it is willing to be a new test site for new approaches including biofiltration - if further funding can be secured.

*Collaboration Type:* Program interaction
*Fiscal Year:* 1998
*Collaborating Organization:* SRS




Biofilter design software was developed for Windows 95/98™ to enable users to quickly and easily determine how various operating parameters will impact their biofilter designs a priori. The user interface is straightforward; data may be copied and then pasted into spreadsheets or presentation packages. Calculation times vary from ~5 seconds to ~5 minutes on Pentium™-class processors. [see Project #73793, renewal of #55013]

*Description:* Biofilter design software was developed for Windows 95/98TM to enable users to quickly and easily determine how various operating parameters will impact their biofilter designs a priori. The user interface is straightforward; data may be copied and then pasted into spreadsheets or presentation packages. We have provided beta-program for operational predictive biofilter to University of California Riverside. ORNL completed further development of a comprehensive two-dimensional predictive model to elucidate mass transfer and kinetic limitations in these systems. This model can be extended to a variety of columnar biofiltration systems by changing appropriate parameters.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborating Organization:* University of California Riverside

## Geochemistry

### Project: 54741

*Title:* Characterization of Contaminant Transport Using Naturally-Occurring U-Series Disequilibria

*PI:* Dr. Michael T. Murrell *Institution:* LANL

*Description:* Consulted regarding uranium measurements at Rocky Flats by contractors for Rocky Flats and the State of Colorado. We later received a small amount of funding to make some measurements for solar pond waters at Rocky Flats. The approach used was similar to that of our EMSP project.

*Collaboration Type:* Consulting *Fiscal Year:* 1999

*Collaborator:* Dave Janecky

*Collaborating Organization:* Rocky Flats Environmental Technology Site, State of Colorado

### Project: 70070

*Title:* Reactivity of Primary Soil Minerals and Secondary Precipitates Beneath Leaking Hanford Waste Tanks

*PI:* Dr. Kathryn L. Nagy *Institution:* University of Colorado

*Description:* Since the late 1950s, leaks from 67 single-shell tanks at the Hanford Site have been detected or suspected, resulting in the release of about 1 million curies to the underlying sediments. The Hanford Tri-Party Agreement calls for the initiation of remediation at the 200 Area tank farms in 2004. There is a risk that these activities may add to and/or mobilize the existing inventory of contaminants in the vadose zone. At issue is the distribution of contaminants beneath the tanks, the processes that led to their current disposition, and the processes that will control their future mobility. The high ionic strength, high pH, and high aluminum concentrations in the tank liquids can significantly alter the vadose zone sediments through dissolution of primary minerals and precipitation of secondary minerals. Data obtained will be directly useful to other EMSP projects addressing contaminant mobility in the vadose zone. The ILAW project and Vadose Zone Characterization project, both run by CH2M-Hill Hanford Group (CHG) at Hanford, are using the lab data on the caustic attack on Hanford sediments to augment similar work that is being performed under direct funding from them. We have also shared the information, samples of Hanford sediment, and recipes for simulated Hanford tank wastes with several other EMSP investigators. Similar interactions are ongoing with other scientists funded by the S&T integration project [Dave Bish and Peter Lichtner at LANL, Carl Steefel and Susan Carroll at LLNL].

*Collaboration Type:* Program interaction *Fiscal Year:* 2001

*Collaborator:* Jiamin Wan, Markus Flury, Jon Chorover, Dave Bish and Peter Lichtner, Carl Steefel and Susan Carroll

*Collaborating Organization:* LBL, WSU-Pulllman, Penn State, LLNL, LANL

### Project: 70081

*Title:* Immobilization of Radionuclides in the Hanford Vadose Zone by Incorporation in Solid Phases

*PI:* Dr. Samuel J. Traina *Institution:* Ohio State University

*Description:* Staff on this project have made significant written contributions to the draft WMA S-SX Tank Farm report due March 31, 2001. These contributions have been in conjunction with the Hanford Science and Technology project (River Protection Program's Hanford Vadose Zone/Groundwater Integration project).

*Collaboration Type:* Consulting *Fiscal Year:* 2001

*Collaborating Organization:* Hanford River Protection Program

### Project: 70146

*Title:* Spectroscopic and Microscopic Characterization of Contaminant Uptake and Retention by Carbonates in Soils and Vadose Zone Sediments

*PI:* Dr. Richard J. Reeder *Institution:* State University of New York at Stony Brook

*Description:* Collaborations are ongoing with two DOE facilities — National Syncroton Light Source at BNL and the Advanced Neutron Source at ANL — to support carbonate mineral characterization and contaminant uptake. Separate co-precipitation experiments with target contaminants will allow an assessment of the effectiveness of uptake during crystallization of calcite, which is favored in the soil and vadose zone as a result of periodic wetting and drying, and also in response to the highly alkaline waste fluids. XAFS spectroscopy will be used to confirm speciation.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001

*Collaborating Organization:* National Syncroton Light Source at BNL and the Advanced Neutron Source at ANL

*Description:* Lanthanides are useful analogs for the behavior of trivalent actinides. Lanthanides are known to sorb strongly onto calcite and partition coefficients, for coprecipitation of trivalent lanthanides with calcite are very large. Hence, calcite may be a very effective sorbent for trivalent actinide species. However, the uptake of trivalent species poses issues of charge balance and coordination in the Ca site in calcite. We have formed a collaboration with University of Central Florida physicist Dr. Robert Peale and graduate student Sandra Withers to characterize the sites in calcite occupied by lanthanides. High-resolution IR spectroscopy will be used in combination with XAFS spectroscopy to determine the number and type of sites. This information will provide the basis for assessing the long-term sequestration of lanthanides and actinides in calcite.

*Collaboration Type:* Program interaction *Fiscal Year:* 2001

*Collaborator:* Dr. R. E. Peale

*Collaborating Organization:* University of Central Florida

*Description:* The overall goals of this project are to determine the role of carbonate minerals in the uptake and long-term sequestration of metal contaminant species, with a focus on soil and vadose zone environments. The metal contaminants studied are relevant to radionuclide waste sources at the Hanford Site, as well as other locations throughout the DOE Complex. One aspect of this research involves determination of the molecular-scale interactions of uranium(VI) species with calcium carbonate minerals. This has implications for sequestration of uranyl species with authigenic calcite via coprecipitation, and the finding may influence uranium remediation techniques that rely on carbonate/bicarbonate leaching. The Principal Investigators have collaborated with LANL researchers C. D. Tait and D. E. Morris using luminescence spectroscopy to identify uranyl species coprecipitated with calcite and aragonite. Luminescence spectra have shown that changes in uranyl coordination occurring during coprecipitation may inhibit uptake by calcite. Luminescence data will be combined with XAFS spectroscopy to assess the molecular coordination of uranyl coprecipitated with calcite. This information will be useful for predicting the long-term retention of uranium(VI) by calcite.

*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* Dr. C. D. Tait and Dr. D. E. Morris
*Collaborating Organization:* LANL

### *Project: 70163*

*Title:* The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica Species to High Concentration: Effects on Neutralization of Leaked Tank Wastes and Migration of Radionuclides in the Subsurface

*PI:* Dr. Andrew R. Felmy *Institution:* PNNL

*Description:* The presence of a wide range of radionuclides, metal ions, inorganic ligands, and organic chelating agents combined with the high base and electrolyte concentration in the Hanford waste tanks creates some unique and difficult problems in modeling the aqueous thermodynamics of these solutions. Solving these problems is important since this can lead to better strategies for tank processing and predictions of subsurface transport. In addition, a large number of scientists and engineers at Hanford and other sites rely on these models for making accurate predictions of tank chemistry. Work is currently being accomplished with the assistance of OLI Systems Inc. to include the Pitzer equations into the ESP tank processing model. ESP is used by all site contractors for simulating tank sludge washing, salt cake dissolution, etc. The inclusion of the Pitzer equations will allow all of the thermodynamic data generated under the EMSP program to be used by these sites.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborating Organization:* OLI Systems Inc.

## Geophysics

### Project: 70052

*Title:* Material Property Estimation for Direct Detection of DNAPL Using Integrated Ground-Penetrating Radar Velocity, Imaging, and Attribute Analysis

*PI:* Dr. John Bradford *Institution:* University of Wyoming

Multi-offset, ground-penetrating radar data acquisition for DNAPL detection at the SRS. [see Project #70052]

*Description:* Many DNAPLs, including chlorinated solvents, have much lower dielectric permittivity and conductivity than water. A contrast in electric properties is induced when DNAPL displaces water in the sediment column resulting in an anomalous GPR signature. The focus of our work is direct detection of DNAPLs, specifically chlorinated solvents, via material property estimation from surface ground-penetrating radar (GPR) data. To directly identify zones of DNAPL contamination, we focus on three aspects of reflected wave behavior - propagation velocity, frequency dependent attenuation, and amplitude variation with offset. Velocity analysis provides a direct estimate of dielectric permittivity, attenuation analysis is used to identify variations in conductivity, and AVO behavior is used to estimate the dielectric permittivity ratio at a reflecting boundary. Areas of anomalously low dielectric permittivity and low conductivity are identified as potential DNAPL source zones. We are working with personnel at the Savannah River and Hanford sites to identify contaminated field areas for both controlled experiments and exploratory investigation.

*Collaboration Type:* Mission directed *Fiscal Year:* 2000

*Collaborating Organization:* Savannah River Technology Center, Hanford Groundwater/Vadose Zone Integration Project

### Project: 70108 (Renewal of Project 55411)

*Title:* Effects of Fluid Distribution on Measured Geophysical Properties for Partially Saturated, Shallow Subsurface Conditions

*PI:* Dr. Patricia A. Berge *Institution:* LLNL

*Description:* We are networking with other current and former EMSP project PI's to plan possible future collaborations on field experiments to test the lab and

theory results of this EMSP project, since this EMSP project is developing methods for improving interpretation of field experiment data used for subsurface imaging. The PI for this project provided advice about geophysical field experiment design for subsurface imaging at the Hanford site, at the Advanced Vadose Zone Characterization Workshop, and in follow-up discussions.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2000
*Collaborator:* C. Carrigan, E. Majer, D. Steeples, R.J. Knight,
*Collaborating Organization:* LLNL, LBL, University of Kansas, Stanford/University of British Columbia

*Description:* The PI for this project was a participant in the Non-invasive Characterization Work Group for the DOE Complex-Wide Vadose Zone Science and Technology Roadmap for Characterization, Modeling, and Simulation of Subsurface Contaminant Fate and Transport. Insights gained in this project and resulting advancements in the area of petrophysics (relating geophysical measurements to hydrological properties and soil composition) have been included in current drafts of the roadmapping report in sections describing the current state-of-the-art of petrophysical relationships.

*Collaboration Type:* Consulting *Fiscal Year:* 2000
*Collaborating Organization:* Department of Energy

### *Project: 70220*

*Title:* High Frequency Electromagnetic Impedance Imaging for Vadose Zone and Groundwater Characterization
*PI:* Dr. Gregory A. Newman *Institution:* Sandia National Laboratories

*Description:* In a collaborative effort, geophysicists from Sandia National Laboratories and the Institute of Geophysics and Meteorology at the University of Cologne in Germany have utilized the world's fastest supercomputer, Ascii-Red, at Sandia to produce the first ever 3D tomograpic reconstruction of a hazardous waste site, near Cologne. This breakthrough allows for high resolution 3D images of the subsurface electrical conductivity/ resistivity using radio waves, and provides a new and important diagnostic tool in accessing the risk such sites pose to groundwater and the environment. To produce the 3D images, significant computer resources were required in the processing of the data. These were obtained through the use of massively parallel computers. With these machines, hundreds to thousands of processors are simultaneously employed in the data processing needed for realistic processing times. The fastest versions of these machines are capable of more than a trillion (1,000,000,000,000) floating point operations per second.

The measurement technique used in the reconstructions is known as the radio magnetotelluric method (RMT), where the data arise from radio transmitters, operating between the 500 kHz to 20 kHz frequency band. With funding provided by the German National Science Foundation, the

Institute has been a pioneer in the development of the method and its application to hazardous waste site characterization in Germany and the European Community, but has been limited in its capability to image the data in three-dimensions, required for high quality risk assessment. While scientists from Sandia have developed such 3D imaging algorithms under the Environmental Management Science Program (EMSP), they have had limited access to high quality field data sets necessary to verify the accuracy and robustness of these imaging schemes. By joint collaboration between the Institute and the laboratories, an important breakthrough has been achieved.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborating Organization:* Institute of Geophysics and Meteorology at the University of Cologne, Germany

## *Health Science*

### *Project: 55033*

*Title:* Characterization of Chemically Modified Hyperthermophilic Enzymes for Chemical Syntheses and Bioremediation Reactions
*PI:* Dr. Brian H. Davison *Institution:* ORNL

*Description:* We have discussed our research and their research with Brian Clark of Enzyme Technologies. They have a crude enzyme solution for oxidative attack of organics. We received a sample of their enzyme solution in February 2000 and hope to run a few preliminary tests.
*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Brian Clark
*Collaborating Organization:* Enzyme Technologies

*Description:* Research developments in the area of biocatalysis in organic solvents are expected to greatly expand the role of bioprocessing in chemical synthesis, fuel processing, and bioremediation technologies. Many biological transformation reactions of interest to DOE site remediation involve species that are only sparingly soluble in aqueous environments. Hence, destruction of these incalcitrant and toxic materials would benefit tremendously if their degradation could be performed in nonaqueous environments. Organic biocatalysis may be motivated by the nature of the substrate itself, or by augmented mass transport, ease of product recovery, or novel reaction pathways afforded by the organic solvent. For instance, polychlorinated biphenyls (PCB's), dense nonaqueous phase liquids (DNAPL's), and manufactured gas plant wastes are sparingly soluble in water, but may be more effectively processed when solubilized by organic liquids. However, naturally occurring enzymes are not soluble in organic solvents, indeed, most spontaneously denature and, depending on the solvent used, typically form inactive and insoluble precipitates. Additionally, the identification that PCB degradation is a critical experiment has been made. The diffculty, however, of bridging fundamental research to deployment, end-user, and focus group needs still exists.
*Collaboration Type:* Program interaction *Fiscal Year:* 1998
*Collaborating Organization:* SRS

*Description:* The objective of the proposed work is to gain a fundamental understanding of the molecular and catalytic properties of enzymes that have been chemically modified so that they are soluble and catalytically active in pure organic solvents. Hydrogenases and redox proteins obtained from hyperthermophiles, which are organisms that grow near and above 100°C, will be investigated as model systems, and the lessons learned will be applied to other hyperthermophilic enzymes with bioremediation potential. The premise for this study is that thermostable enzymes which are both soluble and catalytically active in both water and in a range of organic solvents are optimally suited for bioremediation where substrates of interest are more soluble and may be processed with greater specificity in nonaqueous solvents. Recently, a discussion was held with Brian Clark of Enzyme Technologies. He indicated that their facility has a crude enzyme solution for oxidative attack of organics. Working together, a few preliminary tests have been run on this solution.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* Brian Clark
*Collaborating Organization:* Enzyme Technologies

## *Hydrogeology*

### *Project: 55036*

*Title:* Colloid Transport and Retention in Fractured Deposits
*PI:* Dr. John F. McCarthy *Institution:* ORNL

*Description:* The goal of the project was to identify the chemical and physical factors that control the transport of colloids in water-saturated fractured formations, and develop a generalized capability to predict colloid attachment and detachment based on hydraulic factors, physical structure, and chemical properties. The research targeted multiple scales, including (a) mechanistic description and experiments colloid dynamics in fractures; (b) colloid transport experiments in undisturbed geological monoliths; (c) field-scale colloid transport experiments; and (d) modeling of colloid transport in complex fracture networks.

Fundamental Description Of Particle Transport In Fracture
- Dr. David Walker, Cardiff University, United Kingdom

Colloid Transport In Intact Geological Columns
- Dr. Larry D. McKay, University of Tennessee

Field-Scale Colloid Tracer Migration
- Dr. William E. Sanford, Colorado State University
- Ms. Paige L. Stafford, University of Tennessee

Fracture Network Models of Colloid Transport
- Dr. Motomu Ibaraki, Ohio State University

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborator:* (see description)
*Collaborating Organization:* (see description)

### Project: 60069

*Title:* Least-Cost Groundwater Remediation Design Using Uncertain Hydrogeological Information

*PI:* Dr. George F. Pinder *Institution:* University of Vermont

*Description:* The project seeks to examine the importance of uncertainty in hydraulic conductivity in the least-cost design of groundwater contamination containment systems. The project uses a new conceptual approach to accommodate aquifer parameter uncertainty in optimal groundwater remediation design and introduces a new operations-research technique to solve the optimization problem. The new approach, Robust Optimization, allows for the determination of a robust, lowest-possible cost, pumping design that is consistent with the inherent uncertainty in the hydraulic conductivity field. It also allows for the visualization of how one can trade off excess pumping for enhanced security. Collaborated with BNL for a review of Brookhaven groundwater contamination.

*Collaboration Type:* Consulting *Fiscal Year:* 1999

*Collaborating Organization:* BNL

### Project: 70135

*Title:* Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone

*PI:* Dr. Markus Flury *Institution:* Washington State University

*Description:* This project seeks to improve the basic understanding of colloid and colloid-facilitated transport of contaminants in the vadose zone. The objectives are to determine the structure, composition, and surface charge characteristics of colloidal particles formed under conditions similar to those occurring during leakage of waste typical of Hanford tank supernatants, to characterize the mutual interactions between colloids, contaminant, and soil matrix, to evaluate mobility of colloids through soil under different degrees of water saturation and solution chemistry, and to determine the potential of colloids to act as carriers to transport the contaminant through the vadose zone. We are currently in the process of establishing collaboration with other groups working on colloid transport at DOE sites. This interaction includes coordination of research activities and providing colloidal material for testing purposes, and characterization of colloidal materials.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000

*Collaborator:* John McCarthy and John Selker

*Collaborating Organization:* ORNL and Oregon State University

### Project: 70149 (Renewal of Project 54950)

*Title:* The Dynamics of Vadose Zone Transport: A Field and Modeling Study Using the Vadose Zone Observatory

*PI:* Dr. Charles R. Carrigan *Institution:* LLNL

*Description:* Many releases of chemical solvents or DNAPLS occur at the surface causing the vadose layer to be the first part of a hydrologic system to interact with the contaminant. As the entry point of these chemicals into

a groundwater system, the vadose zone can become a long-term source function for contamination that is metered by natural processes into the underlying saturated zone for further dispersal. However, a contaminant plume does not remain unaffected by the surrounding unsaturated soil. Heterogeneous vadose regimes, such as those containing fractures or other permeability heterogeneities, are the sites of complex interactions between the atmosphere and groundwater. When a volatile contaminant exists as free product or in dissolved form in the vadose environment, upward transport can occur with the contaminant ultimately being vented as a vapor into the atmosphere. It is known that partitioning of a liquid contaminant into the vapor phase can be a very effective means of decontamination. The subsequent transport of the vapor occurs naturally and can be enhanced, for example, by the anisotropy resulting from fractured-matrix-flow paths as well as by certain heterogeneity distributions. Several stages in the transport process are involved in going from a volatile, liquid state contaminant to a contaminant vapor vented at the surface. In a three-year effort, we will investigate the detailed nature of each of these stages of transport in the vadose zones of fractured and heterogeneous regimes with the (1) aid of existing data, (2) new field studies involving dissolved tracer gases and (3) 3-D diagnostic computer simulations that provide a framework to interpret our observations. We will emphasize determining the impact of features specific to a site, that is, the local geology and hydrology, on each stage of the transport process. In particular we want to better understand how the time scales for (1) partitioning contaminants from the liquid to the vapor states and then (2) transporting the vapor out of the vadose regime are dependent on the specific character of a site. Such time-scale information will be important for determining the appropriate response to vadose zone contamination including the option of natural remediation, that is, no response. This information can also be interpreted as a baseline performance criterion for proposed soil-venting schemes. Not least, this work will result in the development of new field methods, involving the injection and analysis of dissolved rare-isotope and chemical-compound tracers, that we anticipate applying to sites at Lawrence Livermore and to the thick, fractured basalt vadose regime at the Idaho National Engineering Laboratory. As such, another (EMSP-EMSP) collaboration based on this philosophy has been completed with Boris Faybishenko at LBNL involving the development of a combined tensiometer/lysimeter system that was developed for use at the VZO.

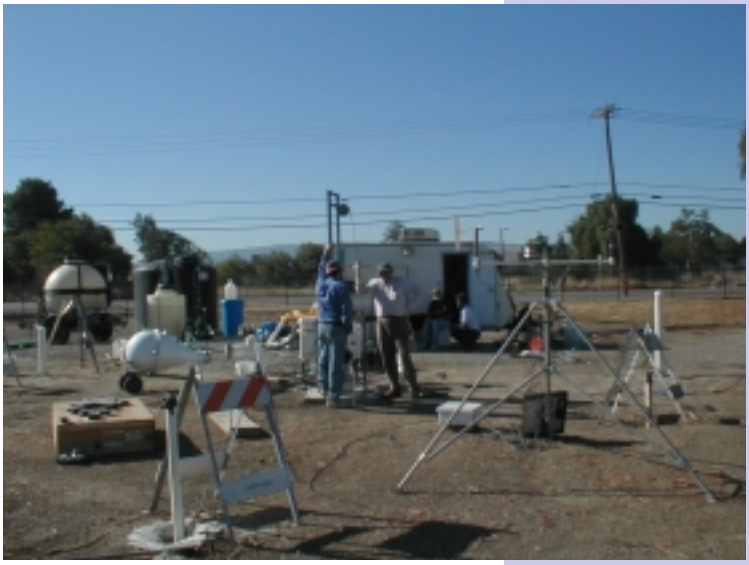
Electric Resistance Tomography (ERT) monitoring capability at the Vadose Zone Observatory (VZO). [see Project #70149, renewal of #54950]

*Collaboration Type:* Program interaction *Fiscal Year:* 2001
*Collaborator:* Boris Faybishenko
*Collaborating Organization:* LBNL

*Description:* In August 2000, we hosted Ernie Majers and Ken Williams (EMSP-EMSP) of LBNL for a test of their cross borehole radar system. The VZO afforded a comparision between a portable in-hole imaging system (radar) and the permanently installed ERT system at the VZO.
*Collaboration Type:* Program interaction
*Fiscal Year:* 2000
*Collaborator:* Ernie Majers/ Ken Williams
*Collaborating Organization:* LBNL

Researchers with the new Electromagnetic Induction Tomography (EMIT) tool, designed for subsurface characterization of a contaminated site. [see Project #70149, renewal of #54950]

*Description:* Collaboration with the Defense Nuclear Facilities Safety Board (DNFSB) is currently ongoing by working with their doctoral and post-doctoral researchers to enhance vadose zone transport and predictive modeling expertise. A stated need of the DOE EM program is a better understanding of basic vadose zone fluid flow and contaminant transport processes for the purpose of making improved estimates of contaminant release rates and fluxes across the vadose zone to the water table at DOE sites such as the tank farms at Hanford.
*Collaboration Type:* Joint interaction
*Fiscal Year:* 2001
*Collaborating Organization:* Defense Nuclear Facilities Safety Board



The VZO site during the infiltration experiment and EMIT tool test. [see Project #70149, renewal of #54950]

*Description:* The VZO has become an official testbed for the National Science Foundation sponsored Center for Subsurface Sensing and Imaging Systems (CenSSIS). The Principal Investigator (C.R. Carrigan) has served as consultant to the CenSSIS program. In November 2000, he gave an invited presentation at the First Industrial Collaboration Conference because of his work with the VZO. CenSSIS is an NSF Engineering Research Center dedicated to developing techniques to image and explore subsurface regimes. You can learn more about CenSSIS at http://www.censsis.neu.edu/. The invited presentation is available by clicking on the flashing link “Nov 13-15 Presentations” on the main CenSSIS webpage.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2000
*Collaborating Organization:* Center for Subsurface Sensing and Imaging Systems (CenSSIS)

*Description:* As a result of CenSSIS, two collaborations are being developed. One involves a proposal on subsurface sensing and data telemetry with Electrical Engineering Professor Qing H. Liu at Duke University, while the other concerns the use of Electric Impedance Tomography (EIT) at the VZO. EIT was developed and refined originally for medical applications by Prof. David Isaacson at Renssaleer Polytechnic Institute and others. Our joint effort will seek to incorporate some of the refinements developed for medical purposes into EM problems involving imaging of contaminant plumes at at the VZO.
*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Prof. Qing H. Liu/ Prof. David Isaacson
*Collaborating Organization:* Duke University/ Renssaleer Polytechnic Institute

*Description:* In September 2000, we carried out a joint experiment at the VZO with researchers from Electromagnetic Instruments (EMI) in Emeryville, CA., Techniscan Inc. in Salt Lake City, Utah, and observers representing SBIR contracts involving Tyndall Air Force Base. The purpose of the collaboration was to test a new Electromagnetic Induction Tomography (EMIT) tool that was designed for subsurface characterization of a contaminated site. The new portable, borehole tool was compared with an existing Electric Resistance Tomography (ERT) system permanently installed at the site. We found that this new device exhibited sensitivity to electrical conductivity changes resulting from plume migration that is comparable to our ERT system. This first test of the borehole EMIT tool was a positive result that is potentially significant for future subsurface characterization studies at contaminated DOE sites.
*Collaboration Type:* Joint interaction *Fiscal Year:* 2000
*Collaborating Organization:* Electromagnetic Instruments (EMI) in Emeryville, CA./ Techniscan Inc. in Salt Lake City/Tyndall Air Force Base

### *Project: 70193*

*Title:* Influence of Clastic Dikes on Vertical Migration of Contaminants in the Vadose Zone at Hanford
*PI:* Dr. Christopher J. Murray *Institution:* PNNL

*Description:* Our project has developed a collaboration with the Science and Technology Effort of the Groundwater/Vadose Zone Integration Project at the Hanford Site. The Groundwater/Vadose Zone Integration Project recently paid the costs of excavating a clastic dike that we were preparing to study. Scientists working with the Groundwater/Vadose Zone Integration Project are also performing drip infiltration tests on the clastic dike and matrix sediments exposed by the excavation. This collaborative research will provide data that will support our EMSP project, as well as the needs of the Hanford Groundwater/Vadose Zone Integration Project.
*Collaboration Type:* Joint interaction *Fiscal Year:* 2000
*Collaborating Organization:* Groundwater/Vadose Zone Integration Project at the Hanford Site

***Project: 70219***

*Title:* Fate and Transport of Radionuclides Beneath the Hanford Tank-Farms: Unraveling Coupled Geochemical and Hydrological Processes in the Vadose Zone

*PI:* Dr. Philip M. Jardine *Institution:* ORNL

*Description:* Philip M. Jardine, PI, is conducting a related project for OBER. Where practical and beneficial, research activities are dovetailed. Technology/ research transfer between the two projects achieves more for each at less cost and on an accelerated schedule because they are strongly linked. Their joint research will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for tank farm restoration.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001

*Collaborator:* Dr. Philip M. Jardine

*Collaborating Organization:* DOE Office of Biological and Environmental Research project, Influence of Coupled Processes on the Fate and Transport of Industrial Mixed Waste Plumes in Structured Media

*Description:* The two projects are resolving the same issues related to the fate and transport of radionuclides beneath the Hanford tank farms. The projects differ only in the type of radionuclides used and the type of geologic formation used. The research projects are strongly linked and will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for tank farm restoration. Technology/ research transfer between the two projects will be beneficial to both.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001

*Collaborator:* Dr. Philip M. Jardine and Dr. John M. Zachara

*Collaborating Organization:* PNNL EM project Geochemical and Hydrological Processes Influencing the Fate and Transport of 90Sr Beneath the Hanford Tank Farms

*Description:* The two projects are working with the same type of media. Where practical and beneficial, research activities are dovetailed. When media samples were collected for this project at Hanford, samples were also collected for Dr. Tokunaga's project, saving time and money. Technology/research transfer between the two projects will be beneficial to both.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001

*Collaborator:* Dr. Tetsu K. Tokunaga

*Collaborating Organization:* EMSP project #70069, Fast Flow in Unsaturated Coarse Sediments

*Description:* Our work is similar to the work done for EMSP Project #70121, "Influence of Calcium Carbonate Grain Coating on Contaminant Reactivity in Vadose Zone Sediments" with different kinds of cores being examined. We are working to develop a technology/research transfer between the two projects that will be beneficial to both since our respective research

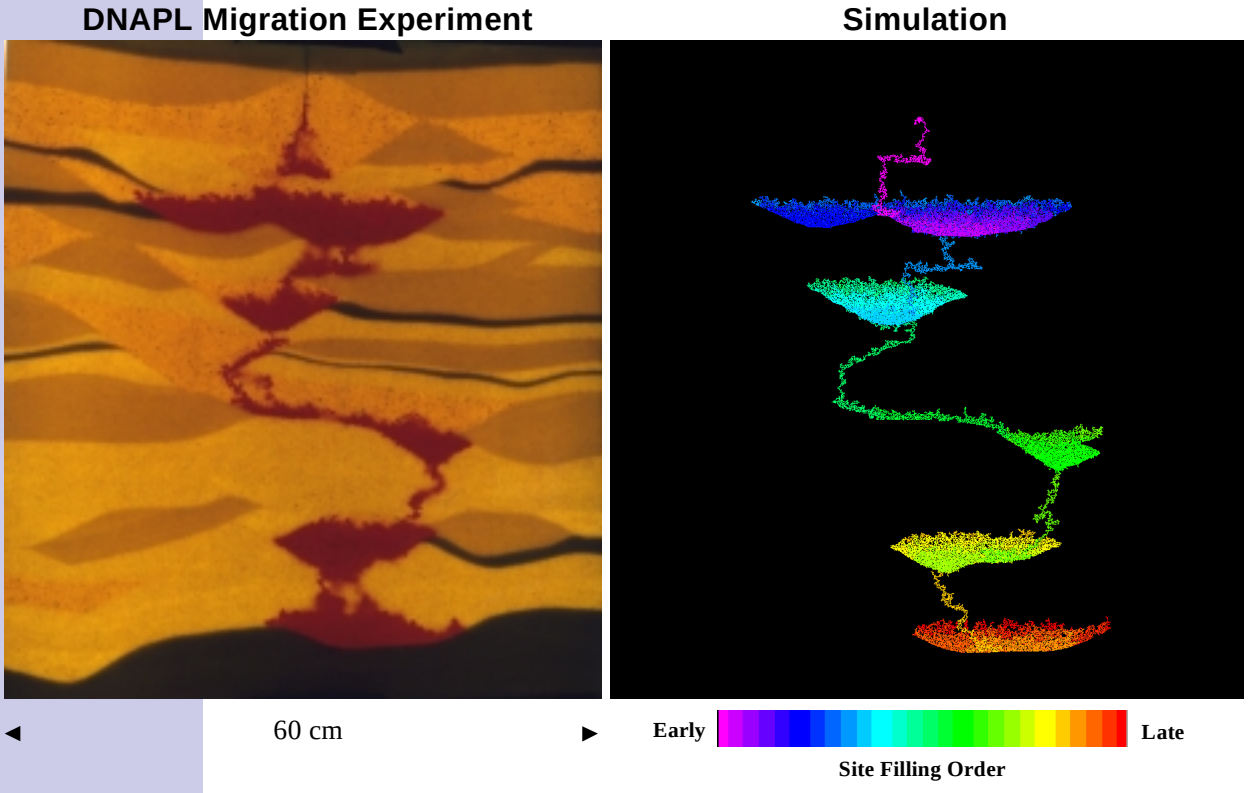
projects are strongly linked and they will jointly provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for tank farm restoration.

*Collaboration Type:* Joint interaction *Fiscal Year:* 2001
*Collaborator:* Dr. John M. Zachara
*Collaborating Organization:* EMSP project #70121, Influence of Calcium Carbonate Grain Coating on Contaminant Reactivity in Vadose Zone Sediments

***Project: 73812 (Renewal of Project 55395)***

*Title:* Physics of DNAPL Migrations and Remediation in the Presence of Heterogeneities
*PI:* Dr. Stephen H. Conrad *Institution:* Sandia National Laboratories - Albuquerque

*Description:* For the Permanganate experiment, we worked with Dr. Jack Istok, a professor at Oregon State. Flushing with potassium permanganate has been investigated as an oxidizer that mineralizes TCE. Jack suspected that the manganese precipitate that forms as a mineralization product cause permeability reduction and thereby inhibit access between the TCE and the permanganate solution and this is precisely what we were able to




Results of a DNAPL migration experiment conducted at Sandia National Laboratories are compared to upscaled percolation modeling. The photo (left) illustrates that the DNAPL(dyed red) migrated downward due to its high density but that aquifer heterogeneities caused significant pooling along the migration path. DNAPL in such a configuration served as the initial condition for remediation experiments. The simulation image (right) compares extremely well with the experiment. [see Project #73812, renewal of #55395]

visually observe in this experiment. The manganese precipitate formed a low permeability ring surrounding the DNAPL pools. Such results had not been seen previously, because for experiments run in uniform media, the DNAPL does not reside in pools. The permanganate oxidation process not likely to be as efficient as initially hoped in cases where DNAPL resides in pools. Perhaps intermittent flushes with a substance to dissolve away manganese precipitate might be possible.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Dr. Jack Istok
*Collaborating Organization:* Oregon State

*Description:* The project involves conducting well-controlled laboratory experiments to better understand the physics of DNAPL migration and remediation in the presence of heterogeneities. The results will be used to test and to continue development of new modeling approaches. In addition, the results of the remediation experiments will be used to test the quantitative performance of remediation design codes within heterogeneous media. We intend to work closely with developers of each remediation approach to attempt to optimize the remedial process and show each technique in its best possible light. Towards that end, Alex Meyer, a professor at Michigan Tech, visited our lab and is collaborating with us on our first series of experiments looking at surfactant mobilization and solubilization of DNAPLs.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Dr. Alex Meyer
*Collaborating Organization:* Michigan Tech

*Description:* For our MA surfactant experiment, we obtained surfactant advice from Alex Meyer and Lirong Zhong. The experiment used the surfactant MA and was designed to maximize solubilization while minimizing mobilization. Contrary to expectation, we observed dramatic mobilization. The DNAPL penetrated the aquitard and became inaccessible to the surfactant. Even though trapping number calculations predict some modest amount of mobilization, failure to account for DNAPL in pools resulted in significantly underestimating the potential for extensive downward mobilization. In observing the mobilization process, we discovered a previously unknown mobilization process that occurs when the surfactant front first encounters a pool. Very different interfacial tensions on either side of the surfactant front result in enhanced drainage of the DNAPL pool. For our particular experimental conditions, due to downward mobilization and penetration of the DNAPL into fine-grained units, introduction of the MA surfactant actually made the problem worse.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Dr. Alex Meyer and Lirong Zhiong
*Collaborating Organization:* Michigan Tech

*Description:* We worked with Dr. Varadarajan Dwarakanath of Duke Engineering to design the tracer test. It occurred to us that the certain conditions provided by our remediation experiments - subsequent to the emplace-

ment of the DNAPL and prior to beginning the remediation - were ideal for performing a tracer test while requiring very little extra work. Partitioning tracer tests are designed to compare the breakthrough of partitioning and non partitioning tracers. Retardation of the tracers that partition into the organic phase provides a means to calculate the mass of DNAPL contained in the region swept by the tracer test. We found that the test worked qualitatively, indicating the presence of DNAPL, but the calculations significantly underestimated the mass of DNAPL in the chamber. We believe that failure to account for the fact that the vast majority of the DNAPL mass existed in large pools resulted in under-prediction of DNAPL mass. When significant DNAPL mass exists in pools, typical tracer flow rates do not allow sufficient time for partitioning/diffusion of the tracers into and out of large pools.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Dr. Varadarajan Dwarakanath
*Collaborating Organization:* Duke Engineering

*Description:* For the Tween surfactant experiment, we obtained surfactant advice from Dr. Kurt Pennell, a professor at Georgia Tech. We obtained much better results using the Tween surfactant. We observed only modest DNAPL mobilization because the Tween surfactant maintains a much higher water/organic interfacial tension. We also observed good solubilization. Complete cleanup was achieved after several pore volumes of flushing. Time lapse animation of this experiment yielded important insights into remediation process.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Dr. Kurt Pennell
*Collaborating Organization:* Georgia Tech Microbial Science

### *Project: 55264*

*Title:* High Resolution Definition of Subsurface Heterogeneity for Understanding the Biodynamics of Natural Field Systems: Advancing the Ability for Scaling to Field Conditions
*PI:* Dr. Ernest L. Majer *Institution:* LBNL

*Description:* The objectives for this project were to develop and apply high-resolution seismic imaging methods for defining physical parameters (lithology, fracture content, fast paths, faults, etc.) that may be controlling flow and transport in naturally heterogeneous material. A primary aspect of the project was to determine if seismic imaging methods could resolve the details necessary to understand the physical heterogeneity controlling microbial behavior. Collaborations are with PNNL and INEEL. PNNL is collaborating in correlating the bacterial behavior to the zones of high permeability detected with the geophysics. INEEL provided the site (TAN) and drilling support as well as collaboration with other EMSP researchers (Colwell and Smith) in understanding the in-situ flow and microbial properties. There were also close collaborations with on site contractors (L. Peterson and T. Woods) in the collection and processing of the data.

*Collaboration Type:* Consulting *Fiscal Year:* 1999
*Collaborator:* Dr. Ardeth Simmons, LBL Yucca Mountain PM
*Collaborating Organization:* Yucca Mountain Project

### *Project: 55416*

*Title:* Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media
*PI:* Dr. Frederick S. Colwell
*Institution:* INEEL

*Description:* The DOE is faced with cleaning up wastes from reactor and weapons production activities during the last fifty years. Many DOE sites have contaminants that are difficult to access due to depth and complex geology and are challenging to degrade using conventional methods. The key objective of this project is to determine the distribution of biologically active contaminant degradation zones in a fractured, subsurface medium with respect to vertical heterogeneities.
*Collaboration Type:* Consulting
*Fiscal Year:* 1997
*Collaborator:* Lance Peterson, Kent Sorenson, and Joe Rothermel
*Collaborating Organization:* INEEL

Aseptic sampling of fractured rock. [see Project #55416]

## *Separations Chemistry*

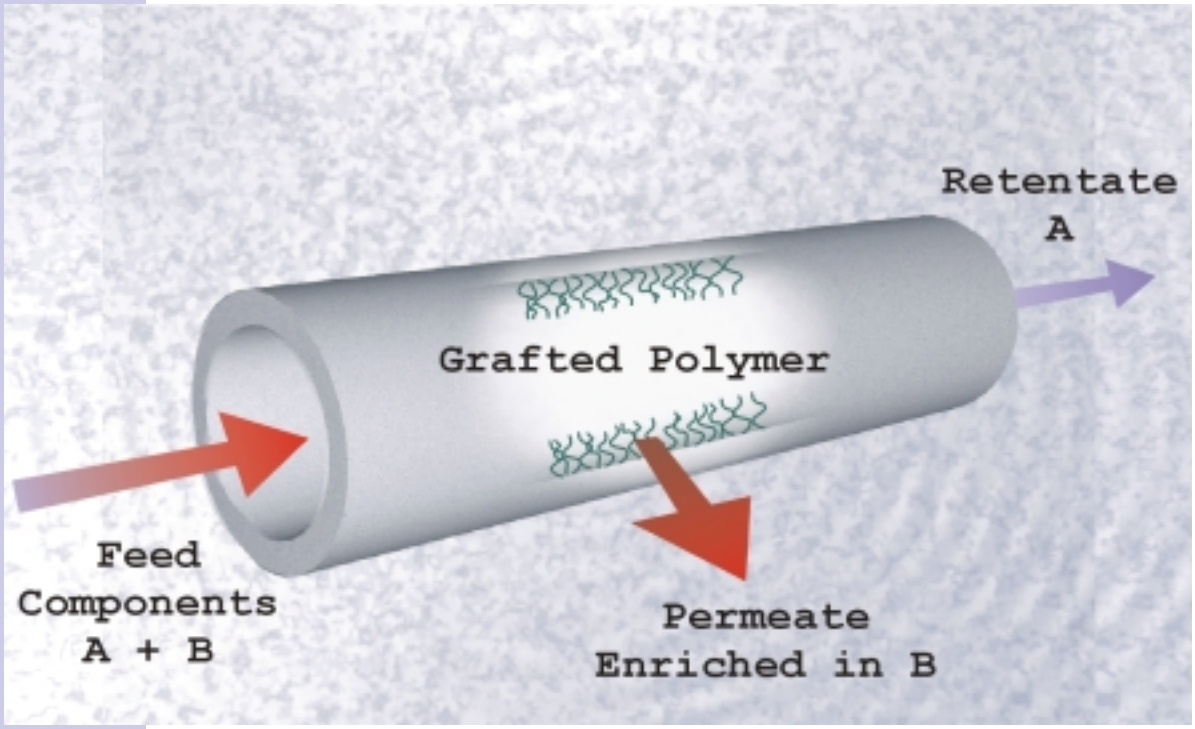
### *Project: 54926*

*Title:* Novel Ceramic-Polymer Composite Membranes for the Separation of Hazardous Liquid Waste
*PI:* Dr. Yoram Cohen *Institution:* University of California at Los Angeles

*Description:* There is a growing need in the areas of hazardous waste treatment, remediation, and pollution prevention for new processes capable of selectively separating and removing target organic species from aqueous streams. Membrane separation processes are especially suited for solute removal from dilute solutions. They have the additional advantage of requiring less energy relative to conventional separation technologies (e.g., distillation, extraction, and even adsorption processes). The major difficulty with current membranes is the poor longevity of polymeric membranes under harsh conditions (high temperature, harsh solvents, and

pH conditions) and the lack of selectivity of ceramic membranes. In our previous work (1996 EMSP project), a first generation of novel polymer-ceramic (PolyCer) composite membranes were developed with the goal of overcoming the above difficulties. The proposed PolyCer membranes are fabricated by a surface-graft polymerization process resulting in a molecular layer of polymer chains which are terminally and covalently anchored to the porous membrane support. We have worked with scientists at the DOE/EMSL facility to characterize the surfaces of our membranes by Atomic Fore Microscopy (AFM) and also by SEM and XPS. We submitted a proposal to EMSL which was accepted. Subsequently, the PI (Dr. Y. Cohen) spent about 4 days at the EMSL facility and his doctoral student (Wayne Yoshida) visited the EMSL facility for a period of three weeks.

*Collaboration Type:* Program interaction *Fiscal Year:* 2000
*Collaborating Organization:* EMSL




Ceramic-Supported Polymer (CSP) Membranes [see Project #54926]

# EMSP Research Transfer

The EMSP provides research resources and results that are intended, in part, to "bridge the gap" between broad fundamental research that has wide-ranging applications such as that performed in the Department's Office of Science, and needs driven applied technology development that is conducted in Environmental Management's Office of Science and Technology. In support of this, the focused research performed in the EMSP is intended to be transferred for utilization by other programs within DOE or to end-users outside the Department.

As research within the EMSP matures, the results from this research should support development of new and innovative ways to reduce risk and cost within EM. In part, the research should address the early, focused research stage of the technology development/deployment cycle for development of new technologies to address cleanup problems within EM. Part of the focus of the EMSP is to integrate the program's research with EM Focus Areas, DOE sites, and commercial interests to support technology development. While much of the research is not yet at a stage of maturity to transfer, many successes have been reported. To date, the reported accomplishments include transfers to:

12Commercializations
2 Deployments
12 Field Tests
3 Focus Areas and Crosscutting Programs
2 Processes.

## Deactivation and Decommissioning

### Inorganic Chemistry

#### Project: 54724

*Title:* Synthesis of New Water-Soluble Metal-Binding Polymers: Combinatorial Chemistry Approach
*PI:* Dr. Barbara F. Smith
*Institution:* LANL

*Description:* Polymer Filtration (PF), which uses water-soluble metal-binding polymers to sequester metal ions in dilute solution with ultrafiltration (UF) to separate the polymers, is a new technology to selectively remove or recover hazardous and valuable metal ions. We have focused on four areas including the development of: (1) synthetic procedures, (2) small ultrafiltration equipment compatible with organic-and aqueous-based combinatorial synthesis, (3) rapid assay techniques, and (4) polymer characterization techniques. We have entered into partnership to use Polymer Filtration in Electroplating industry.

Ultrafiltration unit used in field demonstration for removal of radioactive cations and anions.
[see Project #54724]

*Transfer Type:* Commercialization - Product *Fiscal Year:* 1999
*Contact:* NA
*Transferring Organization:* NA

## Materials Science

### Project: 60363

*Title:* Optimization of Thermochemical, Kinetic, and Electrochemical Factors Governing Partitioning of Radionuclides during Melt Decontamination of Radioactively Contaminated Stainless Steel

*PI:* Dr. James A. Van Den Avyle *Institution:* Sandia National Laboratories

*Description:* We have conducted a successful technology demonstration with the Russians at a site near Krasnoyarsk (K-26), where they electroslag remelted stainless steel reactor coolant piping that was contaminated with Pu and other radionuclides. The resulting metal ingot was fully analyzed and was clean enough to meet Russian criteria for outside reapplication (sale). We are working with them to obtain significant new funding to set up a full scale commercial melt decontamination facility there to recycle stainless steel. We are also paying for a few additional melts there to further characterize the process.

ElectroSlag Remelting (ESR) process for radioactive decontamination of stainless steel scrap for metal recycle. [see Project #60363]

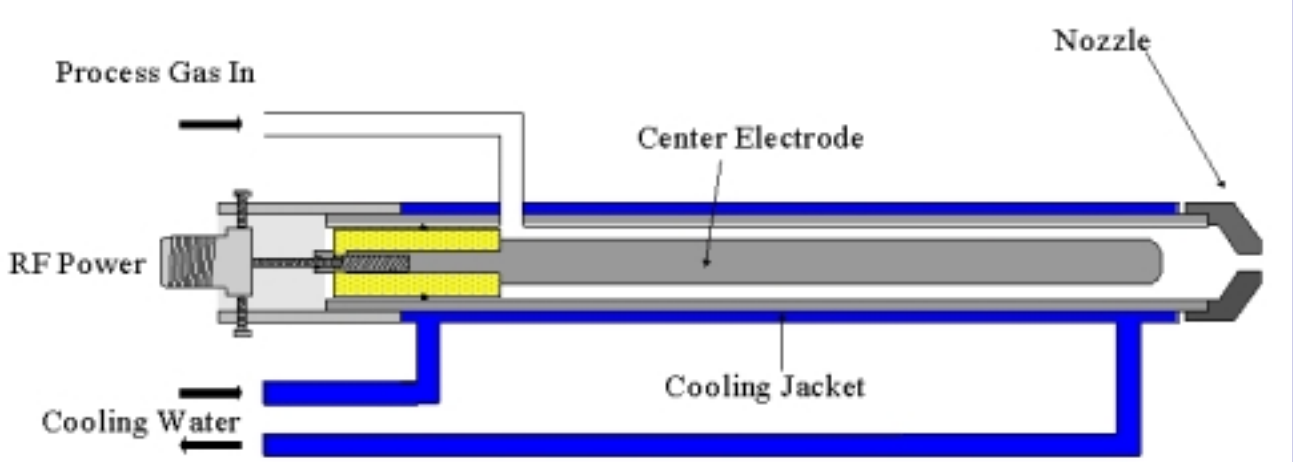
*Transfer Type:* Process
*Fiscal Year:* 1999
*Contact:* James Van den Avyle
*Transferring Organization:* Sandia National Laboratory

### Project: 73835 (Renewal of Project No. 54914)

*Title:* Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces

*PI:* Dr. Robert F. Hicks *Institution:* University of California at Los Angeles

*Description:* After fabricating and testing a prototype plasma decontamination tool, the device will be shipped to the INEEL facility. One post-doctoral scholar will travel to the facility to oversee testing of the plasma device for a specific D&D application. One such application may be the removal of transuranic elements from 1-ft square concrete slabs. In this case, a series of etching experiments will be performed in which the process conditions are varied to obtain the maximum removal rates of TRUs. Air samples will be taken in the vicinity of the process and in the exhaust. These samples will be analyzed to verify that no radioactive waste was released to the surroundings.




Schematic of the first-generation atmospheric-pressure plasma. In this configuration, the process gas is ionized in the annular space between two coaxial electrodes. Then the reactive gas flows out through the nozzle and contacts a work piece placed downstream. [see Project #73835, renewal of #54914]

*Transfer Type:* Field Test *Fiscal Year:* 2000
*Contact:* Larry Whitmill
*Transferring Organization:* INEEL Decontamination and Decommissioning Program

*Description:* We have made arrangements with TA-55, PF-4 Plutonium Processing Facility and CST-12 Materials Testing Laboratory at LANL for additional testing of our device.
*Transfer Type:* Field Test *Fiscal Year:* 2000
*Transferring Organization:* LANL

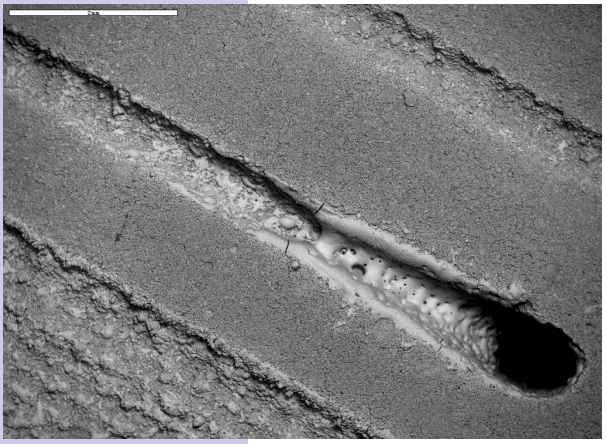
*Description:* The objective of this project is to identify the key physics and chemistry underlying the use of atmospheric pressure plasmas for etching removal of actinides and actinide surrogates. This includes understanding of basic discharge mechanism at atmospheric pressure, gas and surface phase chemistry, and optimization and scale-up effort of atmospheric pressure plasma jet (APPJ). The plasma source developed under this project has been licensed by Plasma Tech, LLC. The company is currently seeking venture capital financing to develop applications for the semiconductor equipment industry.
*Transfer Type:* Commercialization - Product *Fiscal Year:* 2000
*Transferring Organization:* Plasma Tech, LLC

### Separations Chemistry

#### Project: 60283

*Title:* Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation

*PI:* Dr. Michael J. Pellin *Institution:* Argonne National Laboratory



Cement surface following Laser Ablation. [see Project #60283]

*Description:* The objectives of this research are to determine the mechanism and efficacy of laser ablation in removing contaminated surface layers, to understand the chemistry of contaminated concrete surfaces, and to chemically and physically characterize the captured ablation effluent which would become the stored waste. While the focus of this project is on concrete, the technology should be applicable to any surface requiring removal. Efforts are underway to establish a CRADA with Zawtech Inc.

*Transfer Type:* Commercialization - Product

*Fiscal Year:* 1999

*Transferring Organization:* Zawtech Inc.

#### Project: 64912

*Title:* Improved Decontamination: Interfacial, Transport, and Chemical Properties of Aqueous Surfactant Cleaners

*PI:* Dr. David W. DePaoli *Institution:* ORNL

*Description:* Laboratory-scale experimentation has been aimed at determining improved means for removal of organic contaminants using aqueous surfactant cleaners. We have found that through a simple modification of process conditions, the rate of oil removal can be significantly increased. We have communicated, through a non-disclosure agreement, an invention based on our findings with a leading company that produces industrial cleaners. That company has agreed to collaboratively participate in testing of the technology through guidance and evaluation.

*Transfer Type:* Commercialization - Product *Fiscal Year:* 2000

*Contact:* David DePaoli

*Transferring Organization:* Undisclosed at this time

## HEALTH/ECOLOGY/RISK

### Health Science

#### Project: 74050 (Renewal of Project No. 59882)

*Title:* Measurement of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational and Environmental Exposure at US DOE Fernald

*PI:* Dr. Naomi H. Harley *Institution:* New York University Medical School

*Description:* The research is directed to developing state-of-the-art personal and environmental exposure assessment for inhaled radionuclides. The research is conducted at Fernald and the specific nuclides of interest are radon (Rn-222), and thoron (Rn-220) emission from the silos, and thorium-230, 232 airborne aerosol particles from the waste pits. Two new instruments are being used at Fernald, and have been deployed for about 1 year. Together they permit the air concentrations of the gas, the airborne particulates, and their particle size distribution to be measured on a continuous basis. The new instruments developed can have wide application at other DOE sites.

Radon thoron detector, as it would be used in the field of personal monitoring. [see Project #74050, renewal of #59882]

The first insturment is a radon, thoron passive alpha track detector that can be worn or used as an area detector to obtain research quality measurements for modeling or personal exposure assessment. Thoron measurements are not commonly made and little data are available. Measurements at Fernald with simultaneous measurements at research homes in the New York, New Jersey area show that essentially all radon measurements contain a fraction of thoron. NYU is currently seeking a patent for this detector. Plans are to modify the existing model to have 4 detection chambers rather than 3, so that duplicate measurements of both radon and thoron can be made simultaneously.

The second insturment is a particle size analyzer. Although the inhaled particle size is the major determinant of bronchial dose, Fernald is the only site attempting to do particle size distribution measurements. Prior to the development of this instrument, the labor intensive effort needed, as well as the cost, precluded the measurement. The particle size analyzer presently supplies airborne particulate concentration and size data at the waste pits, the soil dryer, and at buildings being removed. A wider network of analyzers is being deployed to study resuspension and transport of particles.

*Transfer Type:* Deployment - Product *Fiscal Year:* 2000
*Transferring Organization:* Department of Energy - Fernald

# HIGH-LEVEL WASTE

## Engineering Science

### Project: 60143

*Title:* Foaming in Radioactive Waste Treatment and Immobilization Processes
*PI:* Dr. Darsh T. Wasan *Institution:* Illinois Institute of Technology

*Description:* The new antifoam has proved to be superior to the current antifoam agent. A series of recent tests was completed to determine whether radioactivity would make the antifoam ineffective by fragmenting it. However, it seems to be resistant to the radiation fields expected in radioactive operations. A vendor has been identified who will produce the antifoam agent for Defense Waste Processing Facility (DWPF). DWPF expects to implement the new antifoam agent before the end of CY00. There is a need for new or improved antifoam agents in a variety of SRS processes including Waste Tank evaporation, Sludge processing, and Salt processing. Other DOE sites with similar evaporation processes, primarily Hanford, ORNL, and INEEL are all in need of better antifoam agents. We need to work closely with them to accomplish these goals.
*Transfer Type:* Deployment - Product *Fiscal Year:* 2000
*Transferring Organization:* Department of Defense - Defense Waste Processing Facility

*Description:* The improved antifoam agent developed by the IIT researchers based on a better understanding of the chemistry, rheology, and physics that lead to the formation of foam during waste processing was successfully tested in laboratory scale experiments at both IIT and SRS and in a pilot plant at SRS. The methodology for developing a new antifoam agent for Defense Waste Processing Facility (DWPF) can now be used to develop other antifoam agents to support other DOE sites, especially Hanford.
*Transfer Type:* Field Test *Fiscal Year:* 2000
*Contact:* Dan Lambert
*Transferring Organization:* SRS

## Separations Chemistry

### Project: 73803 (Renewal of Project No. 55087)

*Title:* Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation
*PI:* Dr. Bruce A. Moyer *Institution:* ORNL

*Description:* The role of the EMSP project in my lab entailed performing a fundamental investigation of the mechanism of cesium extraction so as to understand the nature of the complexes formed between the cesium ion and the extractant molecule. This fundamental information played a crucial role in the successful process development under ESP funding. Indeed, without the fundamental information providing the needed insight at just the right time, the process development would have failed to advance fast enough to meet the emergency need to test new technology at the SRS.

*Transfer Type:* Focus Area - Process *Fiscal Year:* 1999
*Contact:* Bruce Moyer
*Transferring Organization:* ORNL

*Description:* Owing to the high levels of radiation and heat generated by the fission-product Cs-137, efficient cesium separation from high-level wastes (HLWs) has been elevated to extreme importance at Hanford, the SRS (SRS), and Idaho Falls, where multi-billion dollar projects will carry out this and other HLW separations. Referred to as Alkaline-Side CSEX (Cesium Solvent Extraction), the ORNL invention (U.S. Pat. Appl. 60/057,974, September 3, 1998) provides the first practical application of calixarene-crown extractants to treatment of HLWs by solvent extraction. An effective form of the extractant was first synthesized at ORNL and recently transferred to the commercial sector. Batch tests on actual HLW by collaborators at both Hanford and the SRS in the past year have confirmed the effectiveness of the ORNL process, and a 24-stage centrifugal-contactor demonstration at Argonne National Laboratory proved economic viability. Results from the batch and engineering tests showed that stringent requirements of a 40,000-fold reduction in Cs-137 activity in the waste and a 12-fold concentration can be readily met. In addition to meeting these SRS decontamination and concentration needs, key advantages of the ORNL process include the following: (1) The process does not require adjustment of the waste feed stream. (2) Extraction is very selective. (3) Scrubbing and stripping of the solvent can be accomplished with very dilute acidic solutions. (4) The process is compact and involves liquid streams. These advantages reduce costs by minimizing consumption of chemicals, secondary waste production, volume of vitrified waste form, and plant space. The cesium-concentrated stream produced by the process is expected to be so pure that it will require negligible downstream processing and will have negligible impact on the volume of the final vitrified waste form, which is costly to produce and store.

*Transfer Type:* Commercialization - Process *Fiscal Year:* 1999
*Transferring Organization:* IBC Advanced Technologies

*Description:* Westinghouse Savannah River Corporation is conducting tests of alternative technologies for the removal of cesium from its high-level waste and has evaluated the alkaline-side CSEX process as an alternative technology for replacement of the in-tank precipitation process. Successful evaluation will result in further development, scale-up, demonstration, and pilot-scale testing. Ultimately, the goal is implementation in a billion-dollar plant.

We are supplying this customer with information on the alkaline-side CSEX process and responding to customer requests for tests and report results (Note that the PI's ESP task was leading this activity. EMSP's role was in supplying basic scientific information that was useful in development of the process and in understanding process behavior.).

In Nov. and Dec. 1999, the customer at the SRS has shown intense interest in further development of the alkaline-side CSEX process by requesting input for creation of a work-scope for engineering evaluation at the $2-4M level in FY 2000 and FY 2001. In Feb. 2000, DOE approved a $3M task funded through WSRC and led by ORNL for accelerating the development and testing of the alkaline-side CSEX process for possible application in the removal of cesium from high-level salt waste. ORNL, WSRC, and ANL have assembled teams, organizational structure, and plans to carry out this task. This project has been in progress and will continue through June, 2001. Interaction among the ORNL, WSRC, and ANL teams has been daily, with several conference calls each week, numerous reports, numerous presentations, and daily individual interactions. As of September 2000, test results are very positive, and the CSEX process appears competitive with the other two alternative technologies.

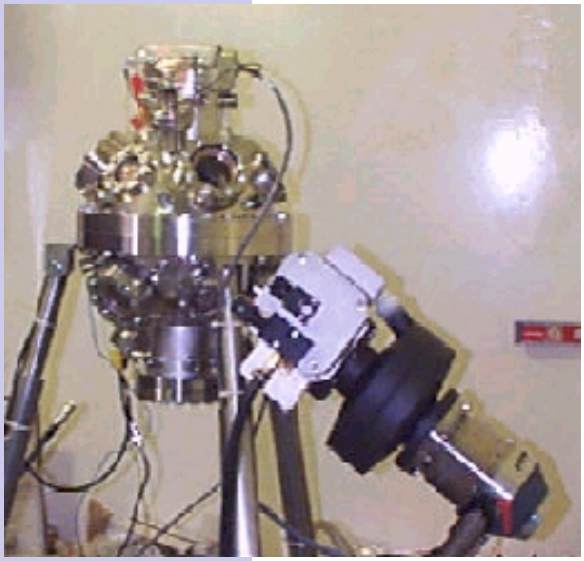
*Transfer Type:* Focus Area - Process *Fiscal Year:* 2000
*Transferring Organization:* Westinghouse Savannah River Corporation

# MIXED WASTE

## Analytical Chemistry & Instrumentation

### Project: 54751

*Title:* High Fluence Neutron Source for Nondestructive Characterization of Nuclear Waste
*PI:* Dr. Mark M. Pickrell *Institution:* LANL



Two commercial partners have applied for a license for the High Fluence Neutron Source, shown here in the laboratory. [see Project #54751]

*Description:* We are addressing the need to measure nuclear wastes, residues, and spent fuel in order to process these for final disposition. One of the primary methods for waste assay is by active neutron interrogation. We plan to improve the capability of all active neutron systems by providing a higher intensity neutron source (by about a factor of 1,000) for essentially the same cost, power, and space requirements as existing systems. We have received 2 request from commercial vendors to commercialize this technology once available.

*Transfer Type:* Commercialization - Product
*Fiscal Year:* 1999
*Contact:* Manfred Frey, Michael Hurwitz
*Transferring Organization:* MF Physics, Inc., Gamma Metrics, Inc.

### Project: 73844 (Renewal of Project No. 60231)

*Title:* Miniature Chemical Sensor Combining Molecular Recognition with Evanescent-Wave Cavity Ring-Down Spectroscopy

*PI:* Dr. Andrew C. R. Pipino *Institution:* National Institute of Standards & Technology - Maryland

*Description:* A entirely new class of chemical sensors is being developed that will enable qualitative and quantitative remote, real-time, optical diagnostics of chemical species in hazardous gas, liquid, and semi-solid phases through a completely novel implementation of cavity ring-down spectroscopy. Negotiations with a commercial partner are in progress.

*Transfer Type:* Commercialization - Product *Fiscal Year:* 1999

*Transferring Organization:* Not disclosed at this time

*Description:* A Cooperative Research and Development Agreement (CRADA) is being negotiated to develop and build prototype, portable, miniature spectrometers, which will be fiber-optic-coupled to inexpensive diode laser sources.

*Transfer Type:* Commercialization - Product *Fiscal Year:* 1999

*Transferring Organization:* Informed Diagnostics, Inc

*Description:* Discussing deployment of miniature spectrometer at the SRS for groundwater monitoring.

*Transfer Type:* Focus Area -Product *Fiscal Year:* 1999

*Contact:* Michael G. Serrato

*Transferring Organization:* SRS

## Separations Chemistry

### Project: 54571

*Title:* Removal of Heavy Metals and Organic Contaminants from Aqueous Streams by Novel Filtration Methods

*PI:* Dr. Nelly M. Rodriguez *Institution:* Northeastern University

*Description:* Graphite nanofibers are a newly developed type of material that can be synthesized by the decomposition of selected hydrocarbons over selected metal particle surfaces. The structural characteristics of the solid can be manipulated by a careful selection of parameters including the catalyst, the reaction conditions and the temperature. Both the size and the morphology of the metal particle have been found to play an important role on the cross-sectional area as well as the orientation of the graphene sheets. It is therefore possible to produce materials

Researcher characterizing sample by TEM. [see Project #54571]

where the platelets are aligned either parallel, perpendicular, or at an angle with respect to the fiber axis. The consequence of the interplay between particle and morphology is that a variety of conformations are possible including tubular, ribbon-like, or structures where only edges of the basal plane are exposed. Graphite nanofibers are usually produced in bulk quantities using unsupported metal powders, having an average particle size of ~1 nm. The cross-sectional area of the resulting fibers exhibit a large range usually between 5 to 100 mm, as a result of uneven fragmentation of the original particles during the reaction. In our current program, we have attempted to generate nanofibers of controlled dimensions in order to produce material having both a high surface area and a high electrical conductivity that results from a long range crystallographic order.

Discussions have been conducted with both Corning Inc. and W. R. Grace, who have expressed an interest in the commercial prospects of the technology being developed in the program at Northeastern University. The synthesis of carbon nanostructures has been optimized at the laboratory scale and it is anticipated that the large scale production of the material will be undertaken by various companies.

*Transfer Type:* Commercialization - Process *Fiscal Year:* 2000
*Transferring Organization:* Corning, Inc. and W. R. Grace

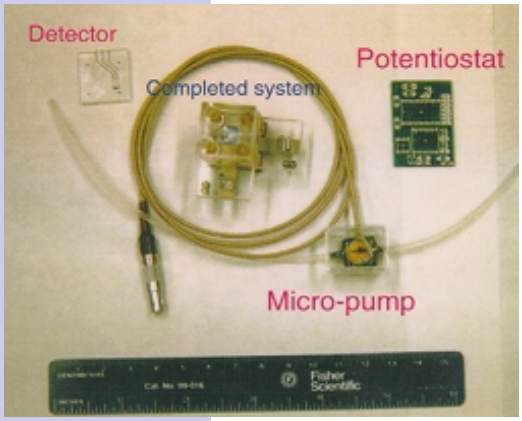
## SUBSURFACE CONTAMINATION

### *Analytical Chemistry & Instrumentation*

#### *Project: 54639*

*Title:* Development of an In-Situ Microsensor for the Measurements of Chromium and Uranium in Groundwater at DOE Sites

*PI:* Dr. Joseph Wang *Institution:* New Mexico State University




NMSU / PNNL Electrochemical Metal Microanalyzer [see Project #54639]

*Description:* This project has led to the replacement of conventional, lab-based, electrochemical stripping protocols and systems with new innovative strategies for field monitoring of trace chromium and uranium, based on micromachined hand-held total stripping analyzers, in-situ sensing devices, and submersible microsystems. These efforts have resulted also in two joint (NMSU-PNL) patents covering the remote-sensor and probe technologies which have been licensed Instrumentation Northwest Inc. (of Richland). New Mexico State University and PNL are working closely on transferring these in-situ metal technologies and realizing their rapid commercialization.

*Transfer Type:* Commercialization - Product *Fiscal Year:* 2000
*Transferring Organization:* Instrumentation Northwest Inc., Richland, WA

## Biogeochemistry

### Project: 55388

*Title:* Stable Isotopic Investigations of In Situ Bioremediation of Chlorinated Organic Solvents
*PI:* Dr. Neil C. Sturchio *Institution:* ANL

*Description:* The purpose of this project was to investigate the potential applications of stable isotope ratio measurements in characterization of the source terms, the transport, and the fate of chlorinated solvents in groundwater aquifers. The approach to this research was threefold: (1) to develop methods for the sampling and isotopic analysis of chlorinated solvents in groundwaters; (2) to perform laboratory experiments to measure equilibrium and kinetic isotope effects associated with biological and physical transformation processes of chlorinated solvents; and (3) to perform field investigations at well-characterized, contaminated aquifer sites to demonstrate the applicability of the isotopic approach in real-world situations. A method for stable isotope analysis of carbon and chlorine in chlorinated aliphatic hydrocarbons developed through this project has been adapted by several laboratories (e. g., University of Nevada, Reno, NV; University of Waterloo, Canada; University of Reading, U.K.; Environment Centre of the Joint European Commission, Ispria, Italy).
*Transfer Type:* Process *Fiscal Year:* 2000
*Contact:* (see description)
*Transferring Organization:* (see description)

*Description:* Methods developed during this project were applied in conjunction with remedial activities for TCE-contaminated groundwater aquifers carried out by Lockheed-Martin Energy Systems, Inc. at the Paducah Gaseous Diffusion Plant in Kevil, KY.
*Transfer Type:* Field Test *Fiscal Year:* 2000
*Contact:* Jay Clausen
*Transferring Organization:* Lockheed-Martin Energy Systems, Inc.

*Description:* Methods developed during this project were applied in conjunction with remedial activities for TCE-contaminated groundwater aquifers carried out by ENSR, Inc. (Westmont, IL) at locations in the Chicago, IL; Kansas City, MO; and Greer, SC areas.
*Transfer Type:* Field Test *Fiscal Year:* 2000
*Contact:* Greg Smith
*Transferring Organization:* ENSR, Inc. (Westmont, IL)

## Engineering Science

### Project: 70088

*Title:* Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone

*PI:* Dr. Baolin Deng *Institution:* New Mexico Institute of Mining & Technology

*Description:* Laboratory investigations conducted over the last several years indicate that reduction and immobilization of chromium in contaminated soil can be achieved in situ through treatment with a diluted hydrogen sulfide gas mixture. The primary chemical reaction of interest associated with these tests involves the reduction of Cr(VI)to Cr(III),with subsequent precipitation as a nontoxic solid product. Immobilization of radionuclides, such as technetium and uranium, and heavy metals, such as mercury and lead are other potential applications of the In Situ Gaseous Reduction (ISGR)approach to vadose zone remediation.

The application of diluted hydrogen sulfide to chromium reduction in the field can be accomplished through the injection of the gas mixture into waste site soils in a central borehole. The gas mixture is then drawn through the waste site by vacuum applied at extraction boreholes located at the site boundary. A successful small scale demonstration of the ISGR approach has been completed at White Sands Missile Range in a joint DOE-DoD field test. This test showed:

- 70%of Cr(VI)in the vadose zone immobilized
- H S gas mixture can be safely handled
- Excess H 2 S is largely consumed by interaction with soil,no releases to the environment

*Transfer Type:* Field Test *Fiscal Year:* 2001

*Transferring Organization:* Department of Energy and Department of Defense

## Geophysics

### Project: 55332

*Title:* A Hybrid Hydrologic-Geophysical Inverse Technique for the Assessment and Monitoring of Leachates in the Vadose Zone

*PI:* James R. Brainard *Institution:* Sandia National Laboratories - Albuquerque

*Description:* The objective of this study is to develop and field test a new, integrated Hybrid Hydrologic-Geophysical Inverse Technique (HHGIT) for characterization of the vadose zone at contaminated sites. This new approach to site characterization and monitoring can provide detailed maps of hydrogeologic heterogeneity and the extent of contamination by combining information from 3D electric resistivity tomography (ERT) and/or 2D cross-borehole ground penetrating radar (XBGPR) surveys, statistical information about heterogeneity and hydrologic processes, and sparse hydrologic data. The project is involved conducting a field test of the

HHGIT at the Sandia/Tech Vadose Zone Facility in Socorro, New Mexico. We are currently processing the data and will be publishing results later this year. Investigators in the project also participated in the Advanced Characterization Workshop at Hanford in January of 2000, and have been in contact with the Tank Focus Area about performing a similar test at the Hanford Reservation.

*Transfer Type:* Field Test *Fiscal Year:* 2000
*Transferring Organization:* Sandia National Laboratory

### *Project: 60162*

*Title:* Enhancements to & Characterization of the Very Early Time Electromagnetic (VETEM) Prototype Instrument & Applications to Shallow Subsurface Imaging at Sites in the DOE Complex
*PI:* Dr. David L. Wright *Institution:* U.S. Geological Survey - Denver

*Description:* The U.S. Geological Survey and the University of Illinois propose to improve the state-of-the-art electromagnetic imaging of the shallow (0 to 5 m) subsurface in conductive media with potential applications to subsurface characterization, landfill stabilization, decontamination/decommissioning, and waste characterization at sites in the DOE complex. We plan to accomplish the research objectives by a combination of hardware and software enhancements to the existing Very Early Time Electromagnetic (VETEM) prototype instrument, physical modeling experiments, numerical forward and inverse modeling, and field demonstrations. We will enhance the existing system with additional antennas, transmitter options, and most likely one or more gradiometer configurations, as well as a modified receiver. The VETEM prototype system has been to INEEL twice since the beginning of our EMSP funding. The first trip, in July 1998, entailed a demonstration at the Cold Test Pit. The second trip was in Nov-Dec of 1998 to do a survey of Pit 9.

*Transfer Type:* Field Test *Fiscal Year:* 1999
*Contact:* Aran Armstrong & George Schneider
*Transferring Organization:* INEEL

### *Project: 73962 (Renewal of Project No. 60115)*

*Title:* Advanced High Resolution Seismic Imaging, Material Properties Estimation and Full Wavefield Inversion for the Shallow Subsurface
*PI:* Dr. Alan Levander *Institution:* Rice University

*Description:* The objective of this project is to develop and test advanced near vertical to wide-angle seismic methods for structural imaging and material properties estimation of the shallow subsurface for environmental characterization efforts. We have conducted a high resolution seismic profile for subsurface characterization at a DNAPL site at a DOD facility in August 1998. Currently, the data is being processed and we are planning to return to the site for additional work.

*Transfer Type:* Field Test *Fiscal Year:* 1999
*Transferring Organization:*

## Hydrogeology

### Project: 55036

*Title:* Colloid Transport and Retention in Fractured Deposits
*PI:* Dr. John F. McCarthy *Institution:* ORNL

*Description:* The rates and extent of colloid and water movement was determined in fractured porous media at Waste Area Group 5 of the ORNL and at a site in Bear Creek Valley near waste disposal areas of the Oak Ridge Y-12 Plant. The data are directly relevant to assessments of risk from the migration of transuranic radionuclides, and in evaluation of remedial options.
*Transfer Type:* Field Test *Fiscal Year:* 2000
*Contact:* Dr. John McCarthy
*Transferring Organization:* ORNL

### Project: 60158

*Title:* Development of Radon-222 as a Natural Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface
*PI:* Dr. Lewis Semprini *Institution:* Oregon State University

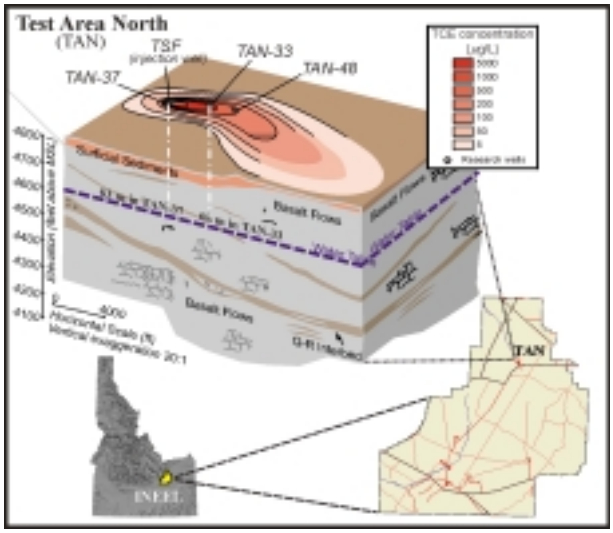
*Description:* The objective of this research is to develop a unique method for using naturally occurring radon-222 as an inexpensive partitioning tracer for locating and quantitatifying nonaqueous phase liquid (NAPL) contamination in the subsurface, and assessing the effectiveness of NAPL remediation. Laboratory, field, and modeling studies are being performed to evaluate this technique and to develop methods for its successful implementation in practice. We have conducted Radon-222 and Surveys at Site-300 at the LLNL. This site is highly contaminated with TCE. The radon results were encouraging, and indicated a zone of NAPL likely existed.
*Transfer Type:* Field Test *Fiscal Year:* 1999
*Contact:* Rolf Halden (925-422-0655 or halden1@llnl.gov)
*Transferring Organization:* LLNL

## Microbial Science

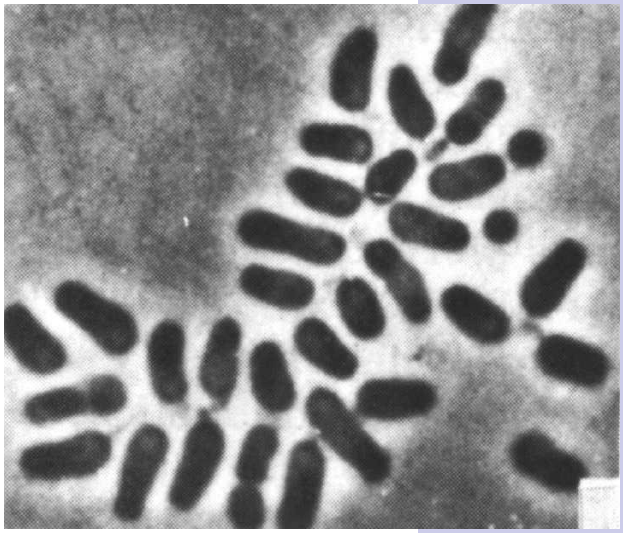
### Project: 55264

*Title:* High Resolution Definition of Subsurface Heterogeneity for Understanding the Biodynamics of Natural Field Systems: Advancing the Ability for Scaling to Field Conditions
*PI:* Dr. Ernest L. Majer *Institution:* LBNL

*Description:* We have been using our technology at the TAN site at INEEL to aid in defining the plume movement and location.
*Transfer Type:* Field Test *Fiscal Year:* 1999
*Contact:* Tom Woods and John Bukowski
*Transferring Organization:* Parsons




Microorganisms with the capability of degrading dissolved TCE in the fractured basalts beneath the INEEL Test Area North are being studied to determine their vertical distribution and to assess how geohydrological factors associated with this complex subsurface environment control their activities. [see Project #55416]



Naturally-occurring TCE-degrading microorganisms may naturally attenuate the TAN TCE plume at low concentrations. [see Project #55416]

### *Project: 55416*

*Title:* Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media
*PI:* Dr. Frederick S. Colwell
*Institution:* INEEL

*Description:* The key objective of this research is to determine the distribution of biologically active contaminant degradation zones in a fractured, subsurface medium with respect to vertical heterogeneities. To determine whether microbial degradation is spatially correlated to preferred flow paths for the contaminant and required electron donors and acceptors we will characterize the biological and abiological properties of cores and samples from multi-level samplers placed in the same borehole. We will use a combination of traditional microbiological methods (e.g., enrichments) and molecular tools to characterize the indigenous microbial communities. During a project that involved coring and well completion of TAN-48 (INEEL) the effect of lactate-induced bioremediation were characterized.
*Transfer Type:* Field Test
*Fiscal Year:* 1999
*Contact:* Lance Peterson, Kent Sorenson, and Joe Rothermel
*Transferring Organization:* LMITCO and Parsons

## Plant Science

Mercury-eating plants developed by this project absorb mercury through their roots, then release it in a less toxic form through their leaves. [see Project #70054, renewal of #54837]

### Project: 70054 (Renewal of Project No. 54837)

*Title:* Phytoremediation of Ionic and Methyl Mercury Pollution
*PI:* Dr. Richard B. Meagher
*Institution:* University of Georgia

*Description:* Our long-term goal is to enable highly productive plant species to extract, resist, detoxify, and/or sequester toxic heavy metal pollutants as an environmentally friendly alternative to physical remediation methods. We have focused this phytoremediation research on soil and water-borne ionic and methylmercury. We engineered several plant species (e.g., Arabidopsis, tobacco, canola, yellow poplar, rice) to express the bacterial genes, merB and/or merA, under the control of plant regulatory sequences. These transgenic plants acquired remarkable properties for mercury remediation. Our project has been so successful that a private company, PhytoWork Inc., has been created.

*Transfer Type:* Commercialization - Business *Fiscal Year:* 1999
*Contact:* Richard Meagher
*Transferring Organization:* PhytoWork Inc.

Hygromycin selection of merA and merB transformed rice shoots and plants from embryogenic calli. A growth comparison of a wild-type to a hyg resistant (HygR) transformed plantlet left two weeks on 30 mg/l hygromycin. [see Project #70054, renewal of #54837]

## Separations Chemistry

### Project: 54926

*Title:* Novel Ceramic-Polymer Composite Membranes for the Separation of Hazardous Liquid Waste
*PI:* Dr. Yoram Cohen *Institution:* University of California at Los Angeles

*Description:* Growing interest by industry in the PolyCer membrane concept is encouraging. With additional optimization work, we are confident that PolyCer membranes will emerge to meet the demand for membranes that retain their structural integrity and longevity under harsh conditions while maintaining the desired selectivity and permeate flux. The approach will pave the way for a rapid tailor-design of pervaporation and UF membranes for organic-aqueous separations. We are currently negotiating with a company called Spinktek Filtration regarding the use of our technology for making non-fouling membranes.

Two other companies (Pervatech in the Netherlands and Asahi Chemical Industry in Japan) signed secrecy agreements with UCLA in connection with our project.

*Transfer Type:* Commercialization - Product *Fiscal Year:* 2000
*Transferring Organization:* Spinktek Filtration

# EMSP Student Research

One goal of the EMSP is to serve as a stimulus to focus the nation's science infrastructure on critical national environmental management problems. One of the primary ways to accomplish this goal is to increase the cadre of scientific expertise available to focus on EM problems. By making opportunities available for Post Doctoral, Ph.D., Masters, and Undergraduate research on EMSP projects, the program achieves this goal. EMSP currently supports the following number of student researchers:

73 Undergraduate Researchers
248 Master Researchers
48 Ph.D. Researchers
156 Post Doctoral Researchers.

The tables below describe the EMSP's accomplishments in the area of undergraduate, graduate, and post-graduate research support as reported in project annual and final reports.

## Deactivation and Decommissioning

### Engineering Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55052 - Advanced Sensing and Control Techniques to Facilitate Semi-Autonomous Decommissioning | 0 | 2 | 4 | 0 |

### Inorganic Chemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54724 - Synthesis of New Water-Soluble Metal-Binding Polymers: Combinatorial Chemistry Approach | 0 | 2 | 0 | 0 |

### Materials Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55380 - In-Situ Spectro-Electrochemical Studies of Radionuclide Contaminated Surface Films on Metals and the Mechanism of their Formation and Dissolution | 0 | 0 | 0 | 1 |
| 59925 - Modeling of Diffusion of Plutonium in Other Metals and of Gaseous Species in Plutonium-Based Systems | 0 | 1 | 0 | 2 |

| | | | | |
|---|---|---|---|---|
| 64896 - Decontamination of Radionuclides from Concrete During and After Thermal Treatment | 0 | 1 | 0 | 0 |
| 64946 - Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic | 2 | 2 | 1 | 0 |
| 73835(Renewal of Project No.54914) - Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces | 0 | 3 | 0 | 2 |

### *Separations Chemistry*

| *Project Number & Title* | *Undergrads* | *Masters* | *Ph.D.s* | *Post Docs* |
|---|---|---|---|---|
| 60041 - Removal of Radioactive Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration | 0 | 2 | 0 | 1 |
| 60283 - Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation | 0 | 0 | 0 | 2 |
| 64912 - Improved Decontamination: Interfacial, Transport, and Chemical Properties of Aqueous Surfactant Cleaners | 3 | 1 | 0 | 0 |
| 64965 - Supercritical Carbon Dioxide-Soluble Ligands for Extracting Actinide Metal Ions from Porous Solids | 0 | 4 | 0 | 0 |

## *HEALTH/ECOLOGY/RISK*

### *Analytical Chemistry & Instrumentation*

| *Project Number & Title* | *Undergrads* | *Masters* | *Ph.D.s* | *Post Docs* |
|---|---|---|---|---|
| 60163 - Investigation of Techniques to Improve Continuous Air Monitors Under Conditions of High Dust Loading in Environmental Settings | 0 | 1 | 0 | 0 |
| 73807(Renewal of Project No.60218) - Rapid Nucleic Acid Analysis for Contaminant Evaluation | 0 | 2 | 0 | 0 |

## Biogeochemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 60015 - Long-term Risk from Actinides in the Environment: Modes of Mobility | 0 | 2 | 0 | 0 |

## Health Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54546 - Engineered Antibodies for Monitoring of Polynuclear Aromatic Hydrocarbons | 0 | 3 | 0 | 3 |
| 54584 - Comparison of the Bioavailability of Elemental Waste Laden Soils Using in vivo and in vitro Analytical Methodology, and Refinement of Exposure/Dose Models | 0 | 0 | 2 | 2 |
| 54684 - Mechanism Involved in Trichloroethylene-Induced Liver Cancer: Importance to Environmental Cleanup | 0 | 5 | 0 | 0 |
| 54940 - Improved Risk Estimates for Carbon Tetrachloride | 1 | 0 | 0 | 0 |
| 55356 - Environmentally-Induced Malignancies: An In Vivo Model to Evaluate the Health Impact of Chemicals in Mixed Waste | 0 | 1 | 0 | 0 |
| 55410 - Determining Significant Endpoints for Ecological Risk Analysis | 0 | 0 | 1 | 1 |
| 73942(Renewal of Project No.59918) - Improved Radiation Dosimetry Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites | 0 | 0 | 0 | 1 |
| 74050(Renewal of Project No.59882) - Measurement of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational and Environmental Exposure at US DOE Fernald | 0 | 1 | 0 | 0 |

### Low Dose Radiation

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 69848 - Adaptive Response Against Spontaneous Neoplastic Transformation in vitro Induced by Ionizing Radiation | 1 | 0 | 0 | 0 |
| 69906 - Markers of the Low-Dose Radiation Response | 0 | 2 | 0 | 3 |
| 69938 - Biological Effects of LLIR and Normal Oxidative Damage: The Same or Different? | 0 | 1 | 0 | 0 |
| 69981 - Mechanisms of Enhanced Cell Killing at Low Doses: Implications for Radiation Risk | 0 | 1 | 0 | 0 |

## HIGH-LEVEL WASTE

### Actinide (Heavy Element) Chemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54595 - f-Element Ion Chelation in Highly Basic Media | 4 | 5 | 0 | 2 |
| 59977 - Synthesis and Characterization of Templated Ion Exchange Resins for the Selective Complexation of Actinide Ions | 0 | 3 | 0 | 0 |
| 65352 - Developing a Fundamental Basis for the Characterization, Separation, and Disposal of Plutonium and Other Actinides in High Level Radioactive Waste: The Effect of Temperature and Electrolyte Concentrations on Actinide Speciation | 1 | 1 | 0 | 2 |
| 65398 - Characterization of Actinides in Simulated Alkaline Tank Waste Sludges and Leach Solutions | 0 | 0 | 0 | 2 |

## Analytical Chemistry & Instrumentation

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55318 - Improved Analytical Characterization of Solid Waste Forms by Fundamental Development of Laser Ablation Technology | 0 | 1 | 0 | 1 |
| 60217 - Optically-Based Array Sensors for Selective in Situ Analysis of Tank Waste | 0 | 0 | 0 | 2 |
| 65340 - Detection and Characterization of Chemicals Present in Tank Waste | 0 | 3 | 0 | 3 |
| 65421 - Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature-Programmed Gas Microsensors | 1 | 1 | 0 | 2 |

## Engineering Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55294 - Superconducting Open-Gradient Magnetic Separation for the Pretreatment of Radioactive or Mixed Waste Vitrification Feeds | 12 | 0 | 0 | 0 |
| 60143 - Foaming in Radioactive Waste Treatment and Immobilization Processes | 0 | 2 | 0 | 1 |
| 60451 - Mechanics of Bubbles in Sludges and Slurries | 0 | 0 | 0 | 1 |
| 65328 - Electrically Driven Technologies for Radioactive Aerosol Abatement | 0 | 3 | 0 | 0 |
| 65371 - Numerical Modeling of Mixing of Chemically Reacting, Non-Newtonian Slurry for Tank Waste Retrieval | 0 | 1 | 0 | 0 |
| 73827(Renewal of Project No.54890) - Non-Invasive Diagnostics for Measuring Physical Properties and Processes in High Level Wastes | 0 | 3 | 0 | 1 |

### Geochemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 60403 - Phase Chemistry of Tank Sludge Residual Components | 0 | 1 | 0 | 0 |

### Geophysics

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55141 - Imaging and Characterizing the Waste Materials Inside an Underground Storage Tank Using Seismic Normal Modes | 0 | 1 | 0 | 0 |

### Inorganic Chemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54646 - Interfacial Radiolysis Effects in Tank Waste Speciation | 0 | 0 | 0 | 2 |
| 54765 - Enhanced Sludge Processing of HLW: Hydrothermal Oxidation of Chromium, Technetium, and Complexants by Nitrate | 4 | 5 | 0 | 0 |
| 54807 - Studies Related to Chemical Mechanisms of Gas Formation in Hanford High-Level Nuclear Wastes | 0 | 3 | 0 | 0 |
| 55137 - Investigation of Novel Electrode Materials for Electrochemically-Based Remediation of High- and Low-Level Mixed Wastes in the DOE Complex | 1 | 2 | 0 | 1 |

### Materials Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54773 - Microstructural Properties of High-Level Waste Concentrates and Gels with Raman and Infrared Spectroscopies | 0 | 0 | 0 | 1 |
| 54982 - Analysis of Surface Leaching Processes in Vitrified High-Level Nuclear Wastes Using In-Situ Raman Imaging and Atomistic Modeling | 5 | 0 | 3 | 0 |

| | | | | |
|---|---|---|---|---|
| 60020 - Stability of High-Level Waste Forms | 0 | 0 | 0 | 1 |
| 73750(Renewal of Project No.54672) - Radiation Effects in Nuclear Waste Materials | 0 | 0 | 1 | 5 |
| 73976(Renewal of Project No.55110) - Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes | 3 | 0 | 2 | 0 |

## *Separations Chemistry*

| *Project Number & Title* | *Undergrads* | *Masters* | *Ph.D.s* | *Post Docs* |
|---|---|---|---|---|
| 54716 - Polyoxometalates for Radioactive Waste Treatment | 0 | 2 | 0 | 0 |
| 54996 - Ionizing Radiation Induced Catalysis on Metal Oxide Particles | 0 | 0 | 0 | 1 |
| 59990 - Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste | 0 | 0 | 0 | 1 |
| 59993 - Dynamic Effects of Tank Waste Aging on Radionuclide-Complexant Interactions | 0 | 1 | 0 | 0 |
| 60017 - Removal of Technetium, Carbon Tetrachloride, and Metals from DOE Properties | 0 | 3 | 0 | 0 |
| 60050 - Chemical Speciation of Inorganic Compounds under Hydrothermal Conditions | 0 | 3 | 0 | 0 |
| 60123 - Potential-Modulated Intercalation of Alkali Cations into Metal Hexacyanoferrate Coated Electrodes | 2 | 2 | 0 | 0 |
| 65339 - Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation and Recycle of Sodium Hydroxide and Sodium Nitrate | 0 | 2 | 0 | 7 |
| 65409 - Electroactive Materials for Anion Separation-Technetium from Nitrate | 0 | 2 | 0 | 0 |

| | | | | |
|---|---|---|---|---|
| 73803(Renewal of Project No.55087) - Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation | 0 | 1 | 0 | 0 |
| 73824(Renewal of Project No.59982) - Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation | 0 | 1 | 0 | 1 |
| 74019(Renewal of Project No.54864) - Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance | 0 | 4 | 0 | 0 |

## MIXED WASTE

### Actinide (Heavy Element) Chemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54679 - Architectural Design Criteria for F-Block Metal Ion Sequestering Agents | 0 | 3 | 0 | 8 |
| 60370 - Rational Design of Metal Ion Sequestering Agents | 0 | 3 | 0 | 3 |

### Analytical Chemistry & Instrumentation

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55171 - Development of Advanced In Situ Techniques for Chemistry Monitoring and Corrosion Mitigation in SCWO Environments | 0 | 1 | 0 | 1 |
| 55247 - Ion and Molecule Sensors Using Molecular Recognition in Luminescent, Conductive Polymers | 0 | 1 | 0 | 9 |
| 60070 - The Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals | 0 | 1 | 0 | 0 |

### Engineering Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54973 - A Novel Energy-Efficient Plasma Chemical Process for the Destruction of Volatile Toxic Compounds | 0 | 1 | 0 | 1 |
| 60326 - Isolation of Metals from Liquid Wastes: Reactive Scavenging in Turbulent Thermal Reactors | 0 | 4 | 0 | 0 |

### Inorganic Chemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54506 - Acid-Base Behavior in Hydrothermal Processing of Wastes | 0 | 1 | 3 | 2 |
| 54828 - Processing of High Level Waste: Spectroscopic Characterization of Redox Reactions in Supercritical Water | 7 | 0 | 0 | 0 |
| 55115 - The Adsorption and Reaction of Halogenated Volatile Organic Compounds (VOCs) on Metal Oxides | 0 | 1 | 0 | 3 |
| 55276 - Fundamental Chemistry and Thermodynamics of Hydrothermal Oxidation Processes | 0 | 0 | 0 | 1 |

### Materials Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55387 - Photooxidation of Organic Waste Using Semiconductor Nanoclusters | 0 | 0 | 0 | 2 |

### Separations Chemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54571 - Removal of Heavy Metals and Organic Contaminants from Aqueous Streams by Novel Filtration Methods | 2 | 1 | 3 | 2 |
| 54770 - New Anion-Exchange Resins for Improved Separations of Nuclear Materials | 0 | 8 | 0 | 2 |

| | | | | |
|---|---|---|---|---|
| 54847 - Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide | 0 | 0 | 0 | 2 |
| 54942 - Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO<sub>2</sub> | 0 | 3 | 3 | 1 |
| 55103 - Utilization of Kinetic Isotope Effects for the Concentration of Tritium | 0 | 0 | 0 | 2 |
| 60096 - Rational Synthesis of Imprinted Organofunctional Sol-Gel Materials for Toxic Metal Separation | 0 | 6 | 0 | 1 |

## NUCLEAR MATERIALS

### Analytical Chemistry & Instrumentation

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 60247 - Miniature Nuclear Magnetic Resonance Spectrometer for In-Situ and In-Process Analysis and Monitoring | 0 | 5 | 0 | 0 |

### Engineering Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 60077 - Development of Nuclear Analysis Capabilities for DOE Waste Management Activities | 0 | 0 | 1 | 0 |

### Materials Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55382 - Determination of Transmutation Effects in Crystalline Waste Forms | 0 | 1 | 0 | 1 |

## SPENT NUCLEAR FUEL

### Geochemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 73691(Renewal of Project No.59960) - Renewal of Direct Investigations of the Immobilization of Radionuclides in the Alteration Products of Spent Nuclear Fuel | 0 | 3 | 0 | 0 |

# SUBSURFACE CONTAMINATION

## Actinide (Heavy Element) Chemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54893 - Research Program to Determine Redox Properties and Their Effects on Speciation and Mobility of Pu in DOE Wastes | 0 | 0 | 0 | 4 |
| 70050 - Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone | 0 | 4 | 0 | 0 |
| 70126 - Collaboration: Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone | 0 | 3 | 0 | 0 |
| 73819(Renewal of Project No.59996) - Plutonium Speciation, Solubilization, and Migration in Soils | 0 | 1 | 0 | 3 |

## Analytical Chemistry & Instrumentation

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54639 - Development of an In-Situ Microsensor for the Measurements of Chromium and Uranium in Groundwater at DOE Sites | 1 | 1 | 0 | 0 |
| 55108 - Monitoring Genetic & Metabolic Potential for In Situ Bioremediation: Mass Spectrometry | 0 | 1 | 2 | 1 |
| 55205 - A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals | 0 | 7 | 0 | 0 |
| 55328 - Novel Analytical Techniques Based on an Enhanced Electron Attachment Process | 0 | 1 | 0 | 0 |
| 70010(Renewal of Project No.54674) - Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone | 3 | 2 | 7 | 0 |

| | | | | |
|---|---|---|---|---|
| 70179 - Radionuclide Sensors for Water Monitoring | 0 | 3 | 0 | 0 |
| 73808(Renewal of Project No.60197) - Microsensors for In-Situ Chemical, Physical, & Radiological Characterization Mixed Waste | 0 | 5 | 0 | 0 |

### *Biogeochemistry*

| *Project Number & Title* | *Undergrads* | *Masters* | *Ph.D.s* | *Post Docs* |
|---|---|---|---|---|
| 54790 - Microbial Mineral Transformations at the Fe(II)/Fe(III) Redox Boundary for Solid Phase Capture of Strontium and Other Metal/Radionuclide Contaminants | 0 | 3 | 0 | 3 |
| 55388 - Stable Isotopic Investigations of In Situ Bioremediation of Chlorinated Organic Solvents | 2 | 1 | 0 | 1 |
| 70063(Renewal of Project No.54666) - Biodegradation of Chlorinated Solvents: Reactions Near DNAPL and Enzyme Function | 0 | 3 | 0 | 0 |
| 70165 - Integrated Field, Laboratory, and Modeling Studies to Determine the Effects of Linked Microbial and Physical Spatial Heterogeneity on Engineered Vadose Zone Bioremediation | 0 | 0 | 2 | 1 |

### *Engineering Science*

| *Project Number & Title* | *Undergrads* | *Masters* | *Ph.D.s* | *Post Docs* |
|---|---|---|---|---|
| 70045 - Investigation of Pore-Scale Processes which Affect Soil Vapor Extraction | 0 | 2 | 0 | 1 |
| 70088 - Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone | 0 | 0 | 0 | 2 |
| 73793(Renewal of Project No.55013) - Biofiltration of Volatile Pollutants: Solubility Effects | 0 | 1 | 0 | 0 |

## Geochemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54548 - The Efficacy of Oxidative Coupling for Promoting In-Situ Immobilization of Hydroxylated Aromatics in Contaminated Soil and Sediment Systems | 5 | 3 | 3 | 2 |
| 54635 - Molecular-Level Process Governing the Interaction of Contaminants with Iron and Manganese Oxides | 2 | 0 | 4 | 0 |
| 54823 - Modeling of Cation Binding in Hydrated 2:1 Clay Minerals | 3 | 3 | 0 | 2 |
| 55014 - Kinetics and Mechanisms of Metal Retention/Release in Geochemical Processes in Soil | 0 | 1 | 0 | 1 |
| 55148 - Hydrologic and Geochemical Controls on the Transport of Radionuclides in Natural Undisturbed Arid Environments as Determined by Accelerator Mass Spectrometry | 0 | 1 | 0 | 0 |
| 70070 - Reactivity of Primary Soil Minerals and Secondary Precipitates Beneath Leaking Hanford Waste Tanks | 0 | 0 | 0 | 1 |
| 70081 - Immobilization of Radionuclides in the Hanford Vadose Zone by Incorporation in Solid Phases | 0 | 7 | 0 | 0 |
| 70121 - The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments | 0 | 1 | 0 | 1 |
| 73745(Renewal of Project No.54585) - Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes | 0 | 3 | 0 | 2 |

| | | | | |
|---|---|---|---|---|
| 73775(Renewal of Project No.55396) - Colloid Genesis/Transport and Flow Pathway Alterations Resulting From Interactions of Highly Reactive Waste Solutions and Sediments in the Vadose Zone | 0 | 0 | 0 | 2 |

## *Geophysics*

| ***Project Number & Title*** | ***Undergrads*** | ***Masters*** | ***Ph.D.s*** | ***Post Docs*** |
|---|---|---|---|---|
| 54655 - Collaborative Research: Hydrogeological-Geophysical Methods for Subsurface Site Characterization | 0 | 6 | 0 | 1 |
| 60162 - Enhancements to & Characterization of the Very Early Time Electromagnetic (VETEM) Prototype Instrument & Applications to Shallow Subsurface Imaging at Sites in the DOE Complex | 1 | 2 | 0 | 1 |
| 70052 - Material Property Estimation for Direct Detection of DNAPL Using Integrated Ground-Penetrating Radar Velocity, Imaging, and Attribute Analysis | 0 | 1 | 0 | 0 |
| 70108(Renewal of Project No.55411) - Effects of Fluid Distribution on Measured Geophysical Properties for Partially Saturated, Shallow Subsurface Conditions | 4 | 0 | 0 | 1 |
| 70115(Renewal of Project No.54699) - The Use of Radar Methods to Determine Moisture Content in the Vadose Zone | 0 | 2 | 1 | 1 |
| 73731(Renewal of Project No.60199) - Automating Shallow Seismic Imaging | 0 | 3 | 0 | 0 |
| 73830(Renewal of Project No.55218) - Seismic Surface-Wave Tomography of Waste Sites | 0 | 0 | 0 | 2 |
| 73962(Renewal of Project No.60115) - Advanced High Resolution Seismic Imaging, Material Properties Estimation and Full Wavefield Inversion for the Shallow Subsurface | 0 | 2 | 0 | 0 |

## Health Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55033 - Characterization of Chemically Modified Hyperthermophilic Enzymes for Chemical Syntheses and Bioremediation Reactions | 0 | 0 | 1 | 5 |

## Hydrogeology

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54576 - On the Inclusion of the Interfacial Area Between Phases in the Physical and Mathematical Description of Subsurface Multiphase Flow | 0 | 0 | 0 | 2 |
| 55036 - Colloid Transport and Retention in Fractured Deposits | 0 | 4 | 0 | 2 |
| 55083 - Behavior of Dense, Immiscible Solvents in Fractured Clay-Rich Soils | 0 | 4 | 1 | 0 |
| 55359 - Chaotic-Dynamical Conceptual Model to Describe Fluid Flow and Contaminant Transport in a Fractured Vadose Zone | 0 | 0 | 0 | 1 |
| 70135 - Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone | 0 | 3 | 0 | 1 |
| 70149(Renewal of Project No.54950) - The Dynamics of Vadose Zone Transport: A Field and Modeling Study Using the Vadose Zone Observatory | 0 | 0 | 0 | 1 |
| 70187 - Quantifying Vadose Zone Flow and Transport Uncertainties Using a Unified, Hierarchical Approach | 0 | 0 | 0 | 1 |
| 73812(Renewal of Project No.55395) - Physics of DNAPL Migrations and Remediation in the Presence of Heterogeneities | 3 | 0 | 1 | 0 |

### Inorganic Chemistry

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55061 - Fundamental Studies of the Removal of Contaminants from Ground and Waste Waters via Reduction by Zero-Valent Metals | 0 | 6 | 0 | 0 |
| 55119 - Phase Equilibria Modification by Electric Fields | 0 | 4 | 0 | 2 |

### Microbial Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 54681 - Dynamics of Coupled Contaminant and Microbial Transport in Heterogeneous Porous Media | 0 | 3 | 0 | 2 |
| 55031 - Genetic Analysis of Stress Responses in Soil Bacteria for Enhanced Bioremediation of Mixed Contaminants | 0 | 1 | 0 | 1 |
| 55105 - Complete Detoxification of Short Chain Chlorinated Aliphatics: Isolation of Halorespiring Organisms and Biochemical Studies of the Dehalogenating Enzyme Systems | 0 | 1 | 0 | 0 |
| 59786 - Design and Construction of *Deinococcus radiodurans* for Biodegradation of Organic Toxins at Radioactive DOE Waste Sites | 0 | 1 | 1 | 2 |

### Plant Science

| Project Number & Title | Undergrads | Masters | Ph.D.s | Post Docs |
|---|---|---|---|---|
| 55097 - Heavy Metal Pumps in Plants | 0 | 0 | 1 | 0 |
| 55278 - Molecular Genetics of Metal Detoxification: Prospects for Phytoremediation | 0 | 1 | 0 | 0 |
| 60271 - Characterization of a New Family of Metal Transport Proteins | 0 | 3 | 0 | 0 |

| | | | | |
|---|---|---|---|---|
| 70054(Renewal of Project No.54837) - Phytoremediation of Ionic and Methyl Mercury Pollution | 0 | 4 | 0 | 1 |
| 73843(Renewal of Project No.55118) - Mechanisms of Heavy Metal Sequestration in Soils: Plant-Microbe Interactions and Organic Matter Aging | 0 | 0 | 0 | 3 |
| 73858(Renewal of Project No.54889) - Chlorinated Hydrocarbon Degradation in Plants: Mechanisms and Enhancement of Phytoremediation of Groundwater Contamination | 0 | 2 | 0 | 2 |

## *Separations Chemistry*

| *Project Number & Title* | *Undergrads* | *Masters* | *Ph.D.s* | *Post Docs* |
|---|---|---|---|---|
| 54122 - A Broad Spectrum Catalytic System for Removal of Toxic Organics from Water By Deep Oxidation | 0 | 2 | 0 | 1 |

EMSP Researcher works with a trickling biofilter that removes dulite organics for contaminated air streams. [see Project #73793, renewal of #55013]

Phase equilibria and interfacial transport may be modified to enhance separations by applying an electric field. A vapor-liquid-equilibrium experiment is shown here. [see Project #55119]

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## TOPICAL WORKSHOPS

Workshops and other interactive forums sponsored by the EM Science and Risk Policy Programs are useful research integration tools because they bring researchers and technology users together. EMSP workshops either center on subject-specific or site-specific topics, using a particular theme to highlight pressing problems within EM, or are held in conjunction with Focus Area reviews and professional society meetings. The objective of tying an EMSP workshop to a Focus Area review is to better define end-user needs so researchers fully understand the site problem for which their research is targeted. Workshops typically feature presentations of the research being conducted by the principal investigators, with industry and/or end-user participation and feedback.

The EMSP Process Relative to the Focus Areas

Such forums allow the EMSP researchers to learn about and discuss actual technology needs with the end-users. At the same time, site representatives and other end-users have an opportunity to hear about science developments directly from those conducting the R&D work. The EM/OST Focus Areas provide the linkage between the EMSP projects and the Department's ongoing waste management and clean-up programs within the Offices of Waste Management (EM-30), Environmental Restoration (EM-40), and Nuclear Materials and Facility Stabilization (EM-60). The five Focus Areas OST currently supports are:

- Deactivation and Decommissioning Focus Area (DDFA)
- Mixed Waste Focus Area (MWFA)
- Nuclear Materials Focus Area (NMFA)
- Subsurface Contaminants Focus Area (SCFA)
- Tanks Focus Area (TFA).

Through communication and cooperation between EM's site end-users, the Focus Areas identify opportunities to integrate the research results of EMSP projects to improve performance and reliability of their baseline clean-up technologies. The Focus Areas also evaluate EMSP projects and results to reveal opportunities to develop breakthrough technologies to solve EM's long-term environmental problems and reduce risk. Figure 1 shows the circular flow of information between the EMSP and the Focus Areas.

Moving research results to application by end-users involves:

- Working with DOE problem holders to identify needs and priorities
- Working with the OST Focus Areas to coordinate activities
- Communicating science results to Focus Area technology developers and EM problem holders.

Dialogue between the end-users and the researchers regarding how the research results can be applied enables sufficient customer understanding of the EMSP projects to "pull" technology down the chain from research to deployment. Focus Areas indicate and facilitate interaction where there is a potential application and provide recommendations for tailoring planned research activities towards Focus Area needs.

The workshops have been very successful and the presentations made by the researchers have been of consistently high quality. Details of the past and planned workshops, including presentations, are available on our program web page (http://emsp.em.doe.gov/workshops/index.htm).

## *Workshop on Integration of End-user needs with Research Projects for EMSP*
## *July 9-10, 1998*
## *Savannah River Site, SC*

The purposes of this workshop were to inform EMSP principal investigators of environmental restoration program needs at SRS, to inform the end-users of currently funded EMSP projects that have relevance to SRS needs, and to determine and plan a program to meet gaps and unmet needs using EMSP research. Among the seventy-five representatives in attendance were EMSP principal investigators; STCG and SCFA end-users; scientists from regional universities, including minority serving institutions and university consortia; DOE contributors; and M&I contractors. The workshop participants received overviews of EMSP and SCFA technologies currently in use at SRS, as well as SRS end-user needs and STCG activities. Tours were available for workshop participants to see SRS needs first-hand.

Three subgroups were formed to develop deployment plans for (1) phytoremediation, (2) DNAPL, characterization, and bioremediation, and (3) metals and rads. The outcome of the phytoremediation subgroup was extremely successful in providing an abbreviated deployment project plan. It was concluded that phytoremediation was a viable technology to meet two stated needs: (1) deploy passive technology for attenuation of VOC, and (2) utilize innovative technologies to replace pump and treat technology. The subgroup proposed three phytoremediation pilot scale demonstrations utilizing loblolly pines, poplar trees, and an aquatic lagoon system. Timelines and cost estimates to process the projects from the science phase through deployment were developed. The DNAPL, characterization, and bioremediation subgroup was less optimistic about the application of the selected southeastern science projects to SRS needs. SRS has large DNAPL plumes where characterization is needed and improved off-gas treatment from vapor extraction technologies is desirable. These selected projects address a gap at SRS. The technologies are 5-9 years away from deployment and currently available technologies allow cleanup to progress. The metals and rads subgroup directed the participating PIs towards discussions with high level waste end-users.

## *First Environmental Management Science Program National Workshop July 27-30, 1998 Chicago, IL*

The first Environmental Management Science Program (EMSP) National Workshop was held July 27-30, 1998 to communicate the progress and plans of all then-active projects. It served as an opportunity for scientists in different disciplines across the program to become acquainted with each other, and to discuss and coordinate research plans. Abstracts for those projects are available in CD-ROM and hardcopy formats and can also be accessed from the EMSP web site at ***http://emsp.em.doe.gov***. The EMSP web site also provides up to date information about ongoing research projects, future events, updated technology needs, and links to other related environmental R&D programs.

## *INEEL Science Integration Workshop*
## *October 20-22, 1998*
## *Idaho Falls, ID*

This site-specific workshop included 101 attendees with interests in four science areas: fractured rock, high level waste (calcine separations), decontamination and decommissioning (D&D), and LandTech. Fractured rock sessions included 12 presentations of ongoing research, followed by two working sessions to discuss opportunities for increased collaboration, as well as the identification of science and technology gaps related to understanding and remediating contaminated fractured rock environments. The D&D group toured the sewage treatment facility at CFA, Pit 9, and the nuclear airplane engine exhibit. The high level waste group toured the calcining facility at INTEC. The LandTech group developed a set of research requirements during their breakout session, and also toured Box Canyon.

Interactions between the PIs and end-users included the following:

- Application of "Lab on a Chip" where Brad Frazee (INEEL) and Greg Collins (Naval Research Laboratory) discussed needs characterization information concerning their important constituents. It was decided that (1) Tom Thiel would get information on the top twelve hitters of "Lab on a Chip" to Greg Collins; (2) Greg would contact the INEEL Sample Management Office in order to test the samples; (3) large scale demonstration of "Lab on a Chip" would be done by Greg and Dick Meservey; and (4) Greg would keep Dick apprised on further research done, with the goal to be using the "Lab on a chip" in the field as part of a large scale demonstration project.

- Mike Savina and Maurice Ross of TRA met with Zawtech, Inc. while in Idaho Falls and they are discussing CRADAs and other industrial partnerships regarding Laser Ablation and Robotics for scabbling.

- Information from INEEL requested transfer of knowledge regarding D&D cost estimates from Brad Frazee. Completed by providing the researchers with the URL that has the information on it.

- Brad Frazee and Dick Meservey will track progress of a novel class of sensors based on light diffraction utilizing polymerized colloidal crystalline arrays for longer-term usage (Sanford Asher). DDFA is interested in field testing a portable sensor.

- Inorganic Ion Exchange Materials for Environmental Restoration research is a promising area because there is an increasing concern regarding water treatment as the size of the reactor being decontaminated and decommissioned increases. The end-users believe there will be a need in the future as commercial power plants are decommissioned. Full-scale membrane filters are needed to cleanup fuel storage basins at the INEEL to warm waste pond disposal limits.

### *Workshop on Integration of End-user needs with Research Projects for EMSP Focus on Deactivation and Decommissioning November 17-18, 1998 Savannah River Site, SC*

The purposes of the workshop were to:

- Increase the awareness of the EMSP principal investigators of the role of the DDFA and thereby increase the applicability of their projects to the D&D mission of DOE,
- Improve SRS knowledge of the EMSP research,
- Identify EMSP projects that have direct usefulness to SRS D&D activities, and
- Determine and discuss EMSP project needs.

Twenty principal investigators and 31 individuals representing the DDFA, end-users, scientists, and DOE program representatives listened to overviews of the EMSP program and the DDFA, discussed lessons learned from the D&D breakout session at the INEEL Workshop and results from the D&D Large Scale Demonstration at the INEEL, and toured SRS's D&D Large Scale Demonstration. The EMSP principal investigators provided a short overview of their projects and afterwards hosted a poster session.

The EMSP PIs gained an improved knowledge of the D&D needs of DOE as a result of the workshop. SRS and selected segments of the DOE complex were informed of the EMSP D&D related research. SRS will provide mentors to several of the projects. Fourteen PIs identified current needs to increase the effectiveness of their research projects. These needs include:

- Representative samples that can be used to test the decontamination process being developed in the laboratory. (A.J. Francis)

- Replicate contaminated metal coupon for quantitative lab tests on biological coatings for removal of contamination radiation. Need to know what is considered "fixed contamination". (Brian Davison)

- Monitoring of mixtures of radionuclides and examining actual samples (e.g. concrete drill samples). Field testing to compare to baseline technologies. (Greg Collins)

- Concrete surface samples and priority of contaminants on concrete (particularly radionuclides). (Brian Spalding)

- Indoor/outdoor location with radioactive airborne contamination to test sampling equipment. Identification of industrial partners. (Piotr Wasiolek)

- More information of the structure and composition of surface contaminants to enable design of more realistic experiments. (Steve Babayan)

- Composition of radioactively contaminated surface layers on pipes and storage tanks, (i.e., type of radionuclides, heavy metal ions, etc.), level of contamination, thickness of surface film. Need 2" x 2" samples. (Carlos Melendres)

- Information on general residues (organics/inorganics/particulates). (R.M. Counce)

- End-users that could benefit from: (1) predictive capability of diffusion between contaminants (plutonium, uranium, etc.) and metal they are in contact with/ contained by (e.g., glove box components and steel storage containers), and (2) a mobile apparatus to detect degree of contamination, chemical and physical characterization of contaminant that has been painted over as opposed to being in a steel container. (Bernard Cooper)

- Database of: (1) alloys/metals commonly contaminated, (2) atmospheric conditions of typical storage and operation in D&D facilities, (3) typical paints/surface coatings that are found on these surfaces, and (4) method and length of time of contamination or exposure to contaminants. (Gary Halada)

These needs range from common samples that could be decontaminated to a mini demonstration facility where representative radioactive samples could be decontaminated with prototype equipment to evaluate the prototype before proceeding to the large scale demonstration facilities provided by the DDFA. Many of the university PIs do not have licenses or facilities to handle radioactive materials, yet need access to these materials for their research.

## *Tanks Focus Area (TFA) Workshop*
## *November 17-18, 1998*
## *Richland, WA*

The Tanks Focus Area (TFA) develops technologies to safely and efficiently remediate radioactive waste stored in underground tanks at four sites nationwide. This work is done by leveraging resources and working with a broad team of experts from industry, national laboratories, government contractors, universities, stakeholders, and U.S. Department of Energy.

The goal of the workshop was to further collaboration between EMSP researchers and TFA end-users in the areas of tank waste characterization, retrieval and pretreatment, and tanks remediation. TFA needs were conveyed to the researchers and interactions were established to transfer the research results to the end-user. Linkage to new and past TFA needs and points of contact were given. EMSP awardees discussed their research plans and received feedback from TFA Technical Integration Managers and safety personnel. Minutes from the breakout sessions summarize TFA questions, recommendations to the researchers, linkages to related tasks, and points of contact.

- *Detection and Characterization of Chemicals Present in Tank Waste* by Dr. P. G. Datskos* (ORNL) and Dr. Sepaniak (Univ. of Tenn.)

  *Questions:*
  - How do you keep the sensor clean?
  - What is the effect of the tank contents (i.e., caustic, acidic, etc.) on the coating?
  - Is there an upper limit for temperatures?
  - How does radioactivity effect the electronics?

  *TFA Recommendation:*
  - There is a need for at-tank rather than in-tank characterization.
  - Look at organics at low-levels (ppm) rather than bulk constituents.
  - Look at suitable analytes.

- *Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature Programmed Gas Microsensors* by Dr. Semancik & Dr. Tarlov (NIST), Dr. McAvoy & Dr. Suehle (U of Maryland) - presented by Richard Cavicchi (NIST)

  *Questions:*
  - Is it reversible?
  - Can it be made quantitative?
  - What are the levels of detection?

  *TFA Recommendation:*
  - No site needs submitted to TFA for tank head-space monitor development in 1995-1998 time period. 8/95 discussions with Hanford project manager for head space gas analysis in tank SY101 indicated that WHC was satisfied with

IR, GC, & $H_2$ chemical cell monitoring of the vent off-gas. CMST pursued the question of in-tank head-space $H_2$ monitoring with the TFA in 5/96 and found no apparent need at Hanford.

– There is a potential application for this technology in the Mixed Waste Focus Area for incinerator off-gas monitoring.

- *Mass Spectrometric Fingerprinting of Tank Waste Using Tunable Ultrafast Infrared Lasers* by Dr. Haglund (Vanderbilt University) and Dr. Wayne Hess (PNNL)

  *Questions:*
  – Can it be made quantitative?

  *TFA Recommendation:*
  – The usefulness of this tool is for quantitative (molecular species) measurements of organics in solids.

- *Electrically Driven Technologies for Radioactive Aerosol Abatement* by O.A. Ezekoye (University of Texas)

  – No linkage found within the TFA.
  – Potential end-users of this technology might be found in the following areas: calcine off-gas, vitrification, and spent nuclear fuel.
  – Other potential applications, such as medical applications, might be found by reviewing the proceedings of the Nuclear Air Cleaning Conference.

- *Precipitation and Disposition of Aluminum-Containing Phases in Tank Waste* presented by Jun Liu representing the collaboration of Baskron, Virden, Wang, and Keefer from PNNL with Hobbs from SRTC and with Dabbs and Aksay from Princeton.

  The TFA asked Jun if he could/would analyze a specimen of the 101 SY tank crust, if he had it. The TFA, Randy Kirkbride, Andy Felmy, and Jun engaged in a discussion about the ability to get this data into the form of information that could be used in the ESP model.

- *Solution Effects on Cesium Complexation with Calixerene Crown Ethers from Liquid to Supercritical Fluids* presented by Chien Wai of the University of Idaho.

  Most of the subsequent discussion centered on the viability of a process that operates at 75 atmospheres in a nuclear environment. This concern has hampered efforts to employ this type of technology in other waste management arenas such as mixed waste. The TFA contends that it is not likely to pass the safety analysis reviews in the foreseeable future. Chien Wai indicated that he would refocus the program to use his experiments to elucidate dissolution mechanisms.

- *Graduate Students* was presented by Yasuo Onishi (PNNL) representing a large number of collaborators: Felmy, Rustad, Recknagle, Michener, Fann (PNNL); Jordon (IBM); Liu (CRAY-SGI Research); and Yuen (University of Minnesota).

TFA asked if differing tank geometries could be included in the model and was reassured that this was the case. TFA indicated that they had funded some tank settling tests for C-106, C-107, and S-106 and would like this data to be used in the model. TFA indicated a desire to have Onishi collaborate with Florida International University in their upcoming line plugging tests.

## *Characterization, Monitoring and Sensor Technology Crosscutting Program (CMST-CP) Annual Review March 8-11, 1999 Gaithersburg, MD*

Thirty-three people attended the EMSP Presentations during the CMST-CP Annual Review. Eighteen attendees were associated with the EMSP and 15 others were from CMST-CP, Focus Areas (FAs), the Nuclear Regulatory Commission, and FETC. There was much interest in the EMSP research by CMST and the FAs.

Eleven EMSP projects and one Wolf-Broido project were presented. There were four research projects on the subject of laser ablation — the researchers were knowledgeable about what the other researchers were doing in the area and formed their own collaborations. A fact sheet describing each project scheduled for presentations was prepared for each EMSP presenter and made available to the CMST-CP Review prior to the presentations. The FA/CP personnel read the information on the fact sheets prior to the EMSP presentations so that they would have some background on the projects and could decide which presentations they wanted to attend. Boris Fabyschenko from LBL distributed a press release on the application of chaos theory to fractured media. Andrew Pipino from NIST displayed a poster on the Evanescent Wave Cavity Ring-Down Miniature Spectrometer in the back of the meeting room. Mark Pickrell from LANL addressed transfer of his mature research project, which has developed a neutron source; two commercial partners have subsequently applied for a license. Four laser ablation research projects were presented (Rick Russo, Scott Goode, Mike Anderson, and Mike Pellin) and CMST expressed interest in perhaps integrating these projects into a follow-on technology development effort.

The banquet was well attended (28 people) and there was a lot of interchange during dinner. The reception afterwards at the hotel provided an opportunity to meet with the researchers and learn more about how to transition their research.

The Environmental Measurements Laboratory (EML) visit was informative and a good opportunity to get to know the DOE/NV CMST manager, the EML personnel, and EMSP researchers and learn about the research conducted by EML. EML will be performing quality assessments and project facilitation for CMST. Close contact between the CMST PIs and the project facilitators keeps the CMST projects on track and aligned with FA/Crosscut needs.

### *Subsurface Contaminants Focus Area (SCFA) Mid-Year Review*
### *April 26-29, 1999*
### *Augusta, GA*

An EMSP room was set-up and over 20 PIs presented posters of their vadose zone work. The poster sessions were well attended. PIs had the opportunity to attend presentations by site personnel discussing current vadose zone cleanup activities.

A special session was held for PIs that was attended by the program manager of the EMSP, Mark Gilbertson, and Tom Hicks from SCFA. Discussions centered around general project descriptions, the SCFA path forward for incorporating EMSP projects in the Focus Area, and PI feedback to Mark Gilbertson. Several of the PIs voiced their support of the recent EMSP research integration efforts including the topical workshops and participation with the Focus Areas.

## *Deactivation and Decommissioning Focus Area (DDFA) Mid-Year Review May 25-27, 1999 Morgantown, WV*

At the request of the DDFA, the Environmental Management Science Program (EMSP) attended and participated in the DDFA Mid-Year Review. Chester Miller of the DOE-HQ made presentations for 21 of the 22 EMSP projects related to DDFA. Dr. Bernard Cooper of the University of West Virginia attended and presented his project. Posters for 8 EMSP DDFA related projects were displayed.

Dr. Cooper indicated that his project is now at a point that he needs someone as a "broker" to help progress it to the next step. He feels that the next step will be to perform field-testing. He is also interested in testing his methods on plutonium/ uranium samples.

Dr. William Stone of NIST expressed interest in Dr. George Xu's presentation on "Real-Time Identification and Characterization of Asbestos and Concrete Materials with Radioactive Contamination". He was provided with a copy of Dr. Xu's presentations, poster and contact information.

The EMSP Staff met with Robert Vagnetti from the DDFA to establish a dialogue on how the EMSP could best support the DDFA in the future and how to make our gap analyses more useful. Mr. Vagnetti indicated that he would be willing to review our current gap analysis and help in efforts for possible research integration.

### *American Chemical Society (ACS)*
### *August 22-26, 1999*
### *New Orleans, LA*

The EMSP will have a strong presence at the ACS Meeting with 120 presentations in 8 technical sessions dedicated to EMSP projects. There will also be 2 tutorials, a plenary session, and 2 poster sessions. A poster on research integration for the EMSP will be presented by EMSP staff. This will provide a forum for researcher interaction among EMSP researchers and non-EMSP funded researchers. A large fraction of the EMSP portfolio addresses research that deals with actinide chemistry issues faced by DOE.

## *Oak Ridge Operations Environmental Management Science Program Workshop September 22, 1999 Oak Ridge, TN*

The purposes of this workshop were to inform EMSP principal investigators of the Oak Operations Office's (ORO) environmental cleanup needs, introduce end-users to EMSP projects that have relevance to ORO needs, and to cultivate collaborations and other relationships between the participants. More than seventy attendees participated in the workshop, including: EMSP researchers; representatives from the Site Technology Coordination Group, Subsurface Contaminants Focus Area, state regulators, and public stakeholder groups; end-users from the major sites administered by the Oak Operations Office; and EMSP staff.

The day's activities began with a short bus tour of two of the three sites that encompass the Oak Ridge Reservation (ORR), the East Tennessee Technology Park and Y-12 Site. The group reconvened at the conference center for a warm Tennessee welcome by the Oak Ridge Operations Office, an introduction to the EMSP, and presentations by the various end-users about their site problems. The sites discussed included the Paducah Gaseous Diffusion Plant, the Portsmouth Gaseous Diffusion Plant, the Y-12 Site, the Oak Ridge National Laboratory (ORNL), and the East Tennessee Technology Park (ETTP, formerly the K-25 Site). After lunch, the participants were guided into one of four breakout sessions where researchers presented their work and discussions about how it related to site needs ensued. The breakout session topics were: 1) D&D Characterization, Decontamination, and Recycle; 2) Soil and Groundwater Treatment; 3) Subsurface Imaging and Characterization; and 4) Bioremediation. Researchers were selected to present their work based on their project's relevancy to ORO cleanup needs.

Interactions between PIs and end-users included the following:

- Dr. A. J. Francis (Brookhaven National Laboratory) and Dr. Gary Halada (SUNY at Stony Brook) began discussions with Gary Person about testing their D&D techniques on materials at ETTP. Their project is titled "Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic Surfaces."

- Dr. Sherman Ponder started discussions with Jerry Harness, representing the Efficient Separations Crosscutting Program, about possible use of Dr. Ponder's unique separations technology. Dr. Ponder's project is titled "Removal of Technetium, Carbon Tetrachloride, and Metals from DOE Properties."

- Dr. Ernest Majer's presentation, "Subsurface High Resolution Definition Of Subsurface Heterogeniety For Understanding The Biodynamics Of Natural Field Systems: Advancing The Ability For Scaling To Field

Conditions", sparked interest by the Subsurface Contaminants Focus Area DNAPLs Product Line Manager, Elizabeth Phillips. They will continue discussions in an effort to collaborate in the future on some bioremediation work.

The site tour generated further interest in seeing more detail about ORNL's subsurface contamination and decontamination and decommissioning projects. A follow-on tour is now being arranged for ORNL principal investigators to meet with team leads for these projects.

## *Nuclear Materials Focus Area EMSP Actinide Chemistry Workshop November 9-10, 1999 Albuquerque, NM*

This workshop brought EMSP principal investigators in contact with representatives and researchers from the Nuclear Materials Focus Area, Nuclear Materials Lead Laboratory, Seaborg Institute, and the Plutonium Center. Research presented during this two-day workshop was designed to highlight current activities related to actinide chemistry of plutonium stabilization, actinides in the subsurface, and actinides solution separations.

Twelve EMSP oral presentations were made, and approximately 20 posters were displayed representing other EMSP research. Topical sessions included in this workshop were:

- Program Overviews
- Clean-up/Decontamination Methods
- Behavior in Groundwater and Soils
- Actinide Behavior in High-level and Other Wastes
- Surveillance, Monitoring, Characterization, and Sensor Development
- Actinide Separations Chemistry and Techniques.

The workshop was attended by more than 40 registered individuals, and due to the close proximity with Sandia National Laboratory, Los Alamos National Laboratory, and The University of New Mexico, numerous non-registered attendees came to selected sessions. As an added activity, attendees were given the opportunity to comment on the EMSP program. At least 10 specific action items were recommended for program improvement.

The workshop ended on a positive note with all participants agreeing that meetings of this type were beneficial and provided opportunities for information exchange related to program needs and areas of promising research and technology development.

## *Kickoff Workshop for the 1999 Environmental Management Science Program Vadose Zone Research Awards November 16-18, 1999 Richland, WA*

These proceedings document the Kickoff Workshop for the 1999 Environmental Management Science Program Vadose Zone Research Awards. The workshop attendees were comprised of researchers, Focus Area representatives, EMSP staff, and science and technology endusers. Three integration teams were formed: (1) Waste/Sediment Lab Experiments and Process Models, (2) Vadose Zone Transport Field Studies, Advanced Characterization, and Transport Modeling, and (3) Monitoring and Remediation at Hanford and Across the Complex. The researchers had the opportunity to listen to talks given by Focus Area representatives, EMSP staff, and science and technology endusers and to present their proposed research plans. The purpose of holding the workshop at the outset of the award process is to give the PIs critical information necessary to direct their research towards the most useful avenues, make available existing data and models, involve the PIs in plans for future vadose zone activities, encourage collaboration among researchers and with endusers, and provide feedback to maximize the benefit of the research. The nucleus of each of these three integration teams will be kept intact through a series of follow-on workshops.

## *Second Environmental Management Science Program National Workshop April 24-28, 2000 Atlanta, GA*

The second Environmental Management Science Program (EMSP) National Workshop was held in Atlanta, GA, from April 24-28, 2000, in order to capitalize on Department of Energy (DOE) investments in environmental science and technology by bringing together environmental management-targeted basic research scientists with Environmental Management Focus Area personnel, site end users, private industry, and other interested parties. EMSP chose the theme *"Science Advancing Solutions"* for this workshop to underscore its commitment to transferring EMSP research results to other Office of Science and Technology programs for further development and ultimate deployment.

The National Workshop brought EMSP Principal Investigators (PIs) together to allow scientists to showcase their research to other scientists, thereby facilitating research synergy. PIs also had the opportunity to meet and interact with DOE site operations and other related Environmental Management Office of Science and Technology (OST) programs personnel (e.g., Focus Areas and Cross-cutting Programs).

The National Workshop was structured with an opening plenary session, followed by breakout sessions, poster sessions, and closing plenary sessions for breakout session summaries and closing remarks. A tour of the Savannah River Site was offered as part of the National Workshop. As a side benefit, a training course on Monitored Natural Attenuation was sponsored by EMSP and presented by the DOE National Environmental Training Office.

One of the most significant goals of the National Workshop was to create research integration opportunities. To achieve this goal, breakout sessions were coordinated and conducted with the Focus Areas and other related programs. The following breakout sessions were conducted:

- Deactivation and Decommissioning Focus Area
- Mixed Waste Focus Area
- National Spent Nuclear Fuel Program
- Nuclear Materials Focus Area
- Subsurface Contaminants Focus Area
- Tanks Focus Area
- Long Term Stewardship
- Low Dose and Risk
- CRESP

Each session chairperson set the agenda for their respective breakout session. Session chairpersons reviewed the EMSP project portfolio, and identified specific projects that contained relevant research with the highest potential for technology development activities. The session chairpersons invited PIs from those projects to present their research to the potential end-users and other PIs.

### *Sensor Initiative Workshop*
### *June 19-20, 2000*
### *Idaho Falls, ID*

A workshop co-sponsored by the Environmental Management Science Program (EMSP) and Long-term stewardship Program was held at the Idaho National Engineering and Environmental Laboratory (INEEL) on June 19 and 20, 2000. The goal of the workshop was to identify research opportunities for sensor development for long-term stewardship. The workshop involved participation, both at the INEEL and via televideo links, by INEEL, Argonne National Laboratory (ANL-West and ANL-East), Fernald, Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), Paducah, Portsmouth, the Savannah River Site (SRS), Sandia National Laboratories (SNL), Nevada, the CMST crosscutting program, and researchers representing twelve EMSP projects. Sensor needs for monitoring and validation applications were identified, functional requirements for the sensors were specified, national laboratory and EMSP research and capabilities were presented, and opportunities for collaboration between the national labs and the EMSP were assessed. The workshop participants agreed to have subject matter experts at their respective sites review and validate the information contained in this report. An overwhelming concensus recommended that a working group be formed to address sensor requirements for long-term stewardship and participate in the roadmap development.